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AFFDL TR-68-63

FA R-1899

INVESTIGATION OF THERMAL-RESISTANT PROPELLANT
FOR EMERGENCY EGRESS ROCKETS

by

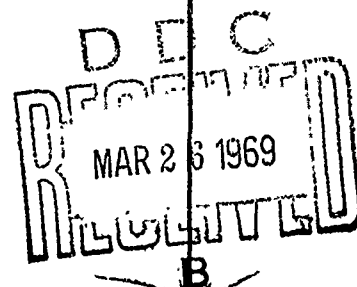
HUGH DOUGLAS MacDONALD, Jr.
DEPARTMENT OF THE ARMY
FRANKFORD ARSENAL
Philadelphia, Pennsylvania 19137

September 1968

TECHNICAL REPORT AFFDL-TR-68-63

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Air Force Flight Dynamics Laboratory
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The distribution of this report is limited because it describes the capabilities of thermal resistant propellants for emergency egress rockets.

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HUGH DOUGLAS MacDONALD, Jr.
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AF Project 1362, Task 136205
USAF MIPR AS-4-109

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Air Force Flight Dynamics Laboratory
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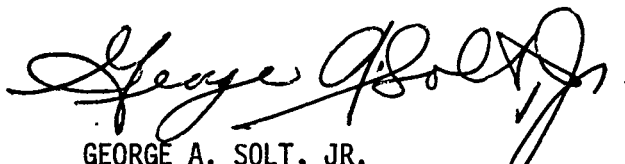
FOREWORD

The program described in this report was performed by Frankford Arsenal, U.S. Army Munitions Command, Philadelphia, Pennsylvania, for the Air Force Flight Dynamics Laboratory (AFFDL), Wright-Patterson Air Force Base, Ohio, under Project 1362, "Crew Escape for Flight Vehicles," Task 136205, within the precept of U.S. Air Force MIPR No. AS-4-109. Captain D. R. Barron, of AFFDL, was the Project Engineer and Mr. H. D. MacDonald, Jr., was the Frankford Arsenal Project Engineer.

Mr. R. F. Vetter, U.S. Naval Weapons Center, China Lake, Calif., performed the work on extrudable fluorocarbon propellants; Mr. J. McDevitt, Naval Ordnance Station, Indian Head, Md., performed the work on KP-Hycar web scale-up.

This report was submitted by the author 29 February 1968.

This technical report has been reviewed and approved:



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ABSTRACT

Selected propellants for escape system rockets were investigated and evaluated at temperatures from -100° to $+400^{\circ}$ F. AK14 Mod I propellant was successfully fired after conditioning for 108 hours between -100° and $+400^{\circ}$ F (a cumulative time of 36 hours at 400° F). PL6670 propellant has had limited testing at 400° F. A KP-Hycar formulation has been scaled up in web, but has not been tested. The test equipment especially designed and constructed for the program has performed reliably.

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SYMBOLS

A	Frequency factor, sec^{-1} .
A_s	Surface area of propellant, in.^2
A_t	Cross-sectional area of nozzle throat, in.^2
a	Radius, in.
C_D	Coefficient of discharge, lbm/lbf sec
C_F	Coefficient of thrust
E	Activation energy, cal/mole
F_m	Maximum thrust, lbf
g	Gravitational constant - 32.2 ft/sec^2
I_{sp}	Specific impulse, lbf-sec/lbm
I_t	Total impulse, lbf-sec
J	Ratio of cross-sectional area of nozzle throat to cross-sectional area of port in the grain
K_N	Ratio of A_s/A_t
k	Specific rate constant, sec^{-1}
p	Pressure, psi
p_{avg}	Average pressure over burn time interval, psi
p_f	Final peak pressure, psi
p_i	Initial peak pressure, psi
p_m	Maximum peak pressure, psi
Q	Heat of reaction (explosion)
R	Gas constant
r_b	Burning rate, in./sec
T	Absolute temperature of peak maximum, $^{\circ}\text{K}$

SYMBOLS (Cont'd)

T_m	Predicted critical temperature, °F
T_l	Maximum surface temperature, °F
t	Time, sec
t_a	Action time interval from 10 percent of maximum peak pressure on rise portion of pressure-time trace to 10 percent of maximum peak pressure on decay portion of pressure-time trace, sec
t_b	Burn time interval from 10 percent of maximum peak pressure on rise portion of pressure-time trace to web burnout, sec
t_b	Burnt time, sec
t_d	Ignition delay time interval from fire pulse to 10 percent of maximum peak pressure on rise portion of pressure-time trace, sec
V_p	Propellant volume, in. ³
v_b	Velocity at burnout in a vacuum, fps
v_o	Velocity at initial condition, fps
W_o	Initial weight, gm
W_r	System weight at burnout, lbm
W_x	Weight after thermal aging, gm
X	Thermal conductivity
y_{max}	Maximum trajectory height, ft
ΔH_{ex}	Heat of explosion (cal/g)
δ	Shape factor
λ	Thermal conductivity
ρ	Propellant density, lbm/in. ³
ρ	Density, gm/cc
ρI_{sp}	Density impulse, lbf-sec/in. ³

SYMBOLS (Cont'd)

- Φ Ratio of propellant volume to system weight at burnout
 Φ Heating rate, °C/min
- $\pi_{p/r}$ Temperature coefficient of pressure at constant ratio of
p/r (Reference is 1000 psig at 70° F), %/°F

INTRODUCTION

The U.S. Air Force requested Frankford Arsenal to investigate and evaluate propellants for use in escape rockets capable of operating over the temperature range of -100° to $+400^{\circ}$ F. The program consisted of a laboratory investigation and a ballistic evaluation of propellants meeting these performance requirements.

The investigation considered both free-standing and case-bonded propellant grains. Although selected propellants were tested in small motors, using subscale grains, they could be scaled up to full size for service type motors.

SCOPE OF WORK

Laboratory Evaluation

During the laboratory investigation, the following objectives were pursued.

1. Determination of thermal stability of propellants exposed to 400° F for periods of 4 hours or longer. This work is described under "TEST PROGRAM AND RESULTS."

2. Relationship between high temperature exposure and chemical decomposition. This work is covered as follows:

AK14 Mod I	-	Reference 1
PL6670	-	Appendix
KP-Hycar		
Thin web propellant	-	Reference
Heavy web propellant	-	No work.

3. Relationship between high temperature exposure and physical deformation. This work is covered as follows:

AK14 Mod I	-	Reference 1
PL6670	-	Appendix
KP-Hycar		
Thin web propellant	-	Reference
Heavy web propellant	-	No work.

4. Autoignition temperature. This work is covered as follows:

AK14 Mod I	-	Reference 1
PL6670	-	Appendix
KP-Hycar		
Thin web propellant	-	Reference 1
Heavy web propellant	-	No work.

5. Elastic and tensile properties of the propellant. Work is covered as follows:

AK14 Mod I	-	Reference 6
PL6670	-	Appendix (at room temperatures only)
KP-Hycar	-	No work.

6. Effects of thermal stress because of temperature cycling over the temperature range. This was done in the ballistic evaluation (see TEST PROGRAM AND RESULTS).

Ballistic Evaluation

During the ballistic evaluation of selected grains, firings of small motors were conducted over the temperature range from -100° to +400° F to determine the standard ballistic parameters. The work is covered as follows:

AK14 Mod I	-	See TEST PROGRAM AND RESULTS.
PL6670	-	See TEST PROGRAM AND RESULTS.
KP-Hycar	-	No work.

PROPELLANT SELECTION

Data generated in the previous thin web effort ^{1*} were used to select propellants for investigation. In that study, rocket propellants were surveyed and the potassium perchlorate (KP) oxidized

* See REFERENCES.

propellants seemed to be the most likely candidates. AK14 Mod I, a propellant used for many years in rocket assisted takeoff of aircraft, was chosen because of its good record in the thin web effort.

Also, a KP-Hycar series had been developed in the thin web effort. However, this was produced by solvent extrusion methods and was limited to thin webs. Work was initiated to produce one of these propellants in a heavier web by solvent extrusion-solventless extrusion techniques.

The survey also indicated that fluorocarbon binders would be thermally resistant. Therefore, a new KP-fluorocarbon propellant was obtained from the Naval Weapons Center (formerly Naval Ordnance Test Station), China Lake, California. This formulation, designated PL6670, is a high density-impulse propellant.

Advanced flight vehicles will probably be equipped with multi-place capsules designed as an integral part of the aircraft.² Because the mission will determine the design of the entire vehicle, the escape system will be a dependent function of the vehicle and the package limit will be essentially volumetric. The system volume limitation can be expressed by the quantity Φ , a constant for a particular system where

$$\Phi = V_p / W_r$$

and V_p is propellant volume;

W_r is system weight at burnout.

Escape rocket performance can be estimated by the velocity at burnout in a vacuum, v_b , which determines the maximum trajectory height, y_{\max} . Assuming a constant thrust rocket which is traveling vertically in a drag-free environment, these parameters can be approximated by

$$v_b \approx I_{sp} \Phi g - g t_b + v_o$$

and

$$y_{\max} \approx (v_b t_b / 2) + (v_b^2 / 2g) + (v_o t_b / 2).$$

For escape rockets, the product ρI_{sp} (or density impulse) is a better performance determinant than I_{sp} propellant quantity. In practice, ρ and I_{sp} are not independent, but are approximately

inversely related. Usually, the density increase is the predominant factor; therefore, an increase in ρ would increase v_b and also y_{\max} .

The use of these parameters can be seen in the following examples.

For a typical ejection seat, where

$$\Phi = V_p / W_r = 103 \text{ in.}^3 / 400 \text{ lbm} = 0.25 \text{ in.}^3 / \text{lbm},$$

$$t_b = 0.4 \text{ second.}$$

An increase of density impulse from the 12 to 18 lbf-sec/in.³ increases the v_b from 84 to 132 fps (Figure 1) and increases y_{\max} from 110 to 290 ft (Figure 2).

For the Mach 4 separable nose capsule,^{3,4}

$$\Phi = V_p / W_r = 1420 \text{ in.}^3 / 2460 \text{ lbm} = 0.575 \text{ in.}^3 / \text{lbm}$$

$$t_b = 0.5 \text{ second.}$$

When $\rho I_{sp} = 12$ for present propellant, $v_b = 206$ fps and $y_{\max} = 710$.

$\rho I_{sp} = 18$ for high density propellant, $v_b = 316$ fps and $y_{\max} = 1630$.

$\rho I_{sp} = 9$ for thermal-resistant propellant, $v_b = 151$ fps and $y_{\max} = 392$.

Escape rockets often have been specified as a retrofit for a normal gun catapult. The rocket, scaled to fit the package of the catapult, is small in diameter (2-3/4 to 3-1/8 in.) but long (55 to 60 in.), an L/D of 17 to 22. Thus, the package is seldom ideal - it is severely volume restricted. Since the thrust level is about 5000 lbf, the mass rate of flow is high, causing throat-to-port (J factor) design hardships. These small sizes, in conjunction with a severe cant angle, limit the size of the throat diameter and the exit cone and, hence, the performance efficiency of the nozzle. The pressure, then, is about 3000 psi to produce 5000 lbf. Although the rocket units for escape capsules are larger, the parameters generally remain the same relative proportion to each other.^{3,4} Even the specification of rockets for new seats and capsules seems to fall in the same historical pattern of the retrofit rocket.

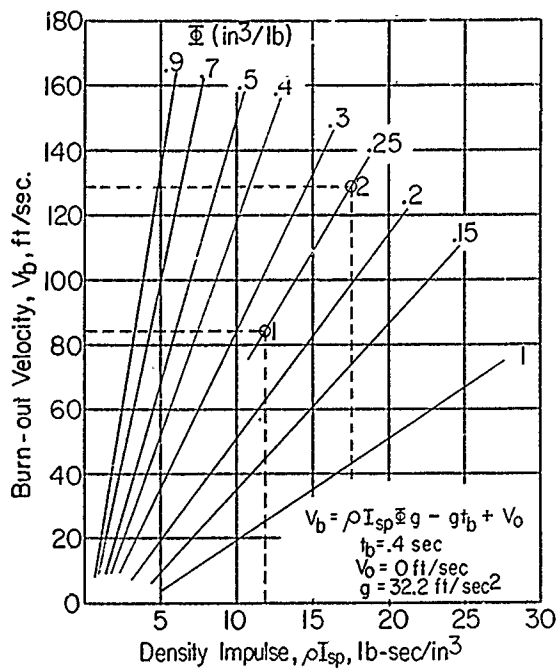


Figure 1. Burnout Velocity vs Density Impulse for Various Values of Φ

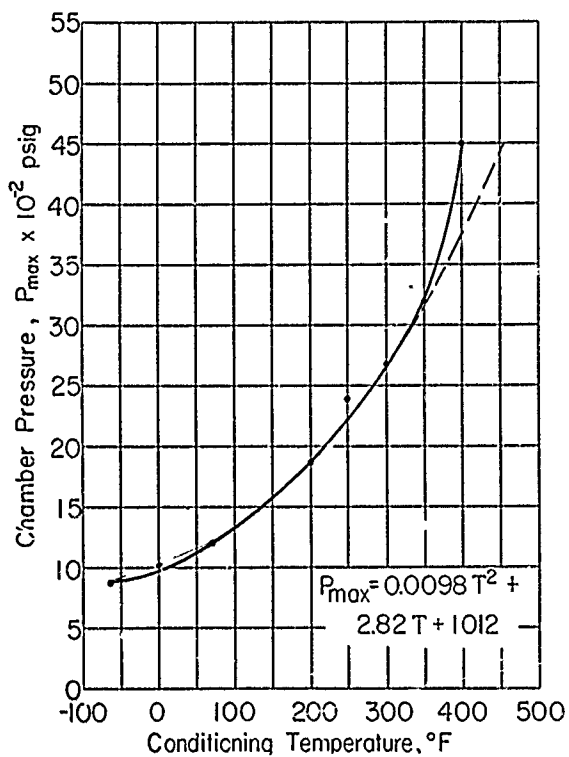


Figure 2. Maximum Trajectory Height vs Burnout Velocity

Although the package is dictated by available space, the performance is dictated by physiological limits.⁵ The maximum allowable acceleration is 24 g (0.1 sec duration), but practice has limited acceleration to 12 or 15 g (0.5 sec duration) at 70° F. Thus, a 400 lbm seat has a 5000 lbf thrust of 12 g and a 2400 lbm capsule has an average of 36,000 lbf thrust of 15 g (0.5 sec duration).

The military specification (MIL-C-25918) requires performance from -65° to +200° F, but advanced flight vehicles may require both resistance and operation throughout a wider temperature range. Where thermal-resistant propellants are not available for a specific application, relocation of the device or thermal protection of the propellant by insulation or refrigeration may be a more practical solution than the development of thermal-resistant propellant (Ref 2, pp 161-162).

In summary, propellant objectives are:

Thermal resistance of 400° F for 4 hours

High density impulse of 18 lbf-sec/in.³

High rocket pressure of 3000 psi

Good physical properties

Low burning rate exponent

Low temperature dependency, π_k

Mesa, or plateau, characteristics.

DESIGN AND CONSTRUCTION OF TEST MOTOR-CONDITIONING CHAMBER SYSTEM

The conditioning chamber is designed to cover the -100° to +400° F temperature range and allow extended storage of the rocket motor, followed by in-place firing. The system is operated remotely for extended periods of time and is nonhazardous to personnel in the adjacent area. If a malfunction were to occur, no debris or shrapnel would be released.

The control system chosen is a capillary type manufactured by Brown Instrument Division, Minneapolis-Honeywell Regulator Co. A plastic cam can be cut to program most of the cycles that would be desired. However, the stall angle of the cam follower

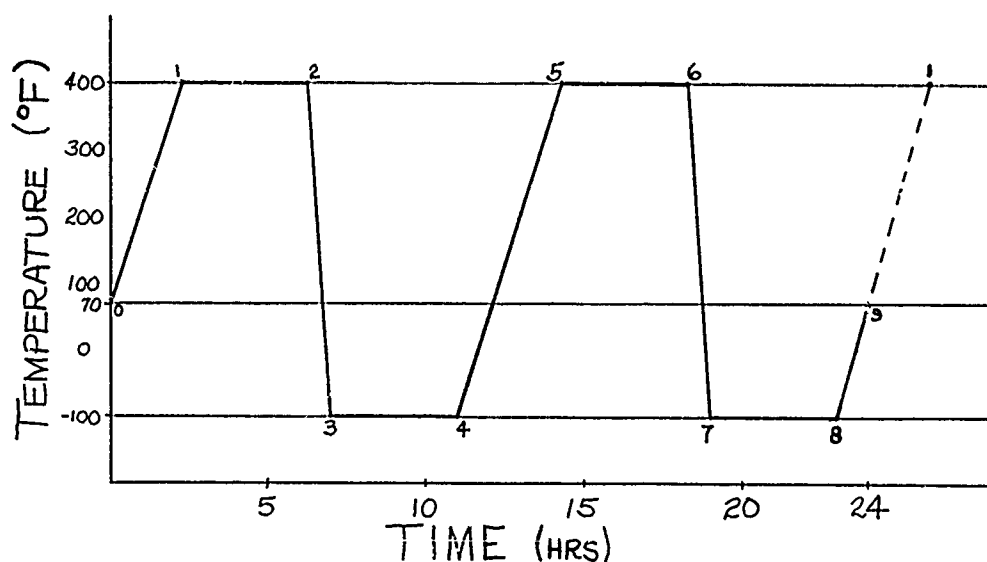
on the rise, or heating, portion of the cycle limits the rate of rise. Faster rise times can be accomplished by hand operation or by other available control systems. The cam profile is shown in Figure 3.

To avoid restriction on sources or types of propellant, the motor allows loading of free-standing unrestricted grains, cartridge-loaded restricted grains, and case-bonded grains (Figure 4). For convenience, the motor is scaled smaller than present escape rocket motors. The data acquired are pressure-time, single component thrust-time, and temperature-time (Figure 5). Vibration and humidity environments are not included, but could be added.

Several conditioning chamber designs were considered: homemade, custom designed commercial, modified commercial stock, and electric heater wire and cooling coils wrapped around the motor. A modified commercial stock unit with liquid CO₂ cooling was chosen as the most economical (Figure 6). The test motor is attached to a load cell on the test bay floor by a cooling column which passes through an access port in the oven floor. Rocket exhaust gases pass through another access port in the chamber roof (Figure 7).

The main door, with control interlock switch, is provided with pressure release latches and a removable receiver cage so that it serves as the blast release and catcher (Figure 8). The controller (Figure 9), a capillary sensor with a plastic cam programmer, is mounted separately from the chamber on the other side of the barricade (Figure 10). An electronic controller can also be used remotely. All the changes to the conditioning chamber were selected from modular packages offered by the manufacturer. Thus, the investment in expendable portions of the equipment was held to a minimum.

Motor design was coordinated with the conditioning chamber. The motor criteria, as stated before, required that there be no debris or shrapnel from a malfunction. Therefore, nozzle shear rings were ruled out. To handle overpressure or deflagration, the motor is constructed like a compressor head. Tie rods are used to attach the head and nozzle block against the motor tube. The tie rods can be torqued to a preset dump pressure value and the deformation of the tie rod is nearly equal to the deformation of the motor tube. The dump pressure is a function of maximum conditioning temperature (Figure 11). At the preset dump pressure, the deformation of the motor tube is relaxed, the head seal is immediately broken, and the round terminates. Of course, the dump value stress is lower than the yield stress in the tie rods.



- t_0 - t_1 Control Capability (assume $2\frac{1}{4}$ hrs)
- t_1 - t_2 Stabilized Oven Temperature (4 hrs @ $400^\circ\text{F} + 5^\circ\text{F}$)
- t_2 - t_3 Control Capability (assume $\frac{3}{4}$ hrs)
- t_3 - t_4 Stabilized Oven Temperature (4 hrs @ $-100^\circ\text{F} + 5^\circ\text{F}$)
- t_4 - t_5 Control Capability (assume $3\frac{1}{4}$ hrs)
- t_5 - t_6 Stabilized Oven Temperature (4 hrs @ $400^\circ\text{F} + 5^\circ\text{F}$)
- t_6 - t_7 Control Capability (assume $\frac{3}{4}$ hrs)
- t_7 - t_8 Stabilized Oven Temperature (4 hrs @ $-100^\circ\text{F} + 5^\circ\text{F}$)
- t_8 - t_9 Control Capability (assume 1 hr)
- t_9 End of 24-hr Cycle: $+70^\circ\text{F}$

The assumed rise and fall times for control capabilities may be adjusted to obtain a smoother cam contour between time t_8 and t_1 .

Figure 3. Cam Instructions

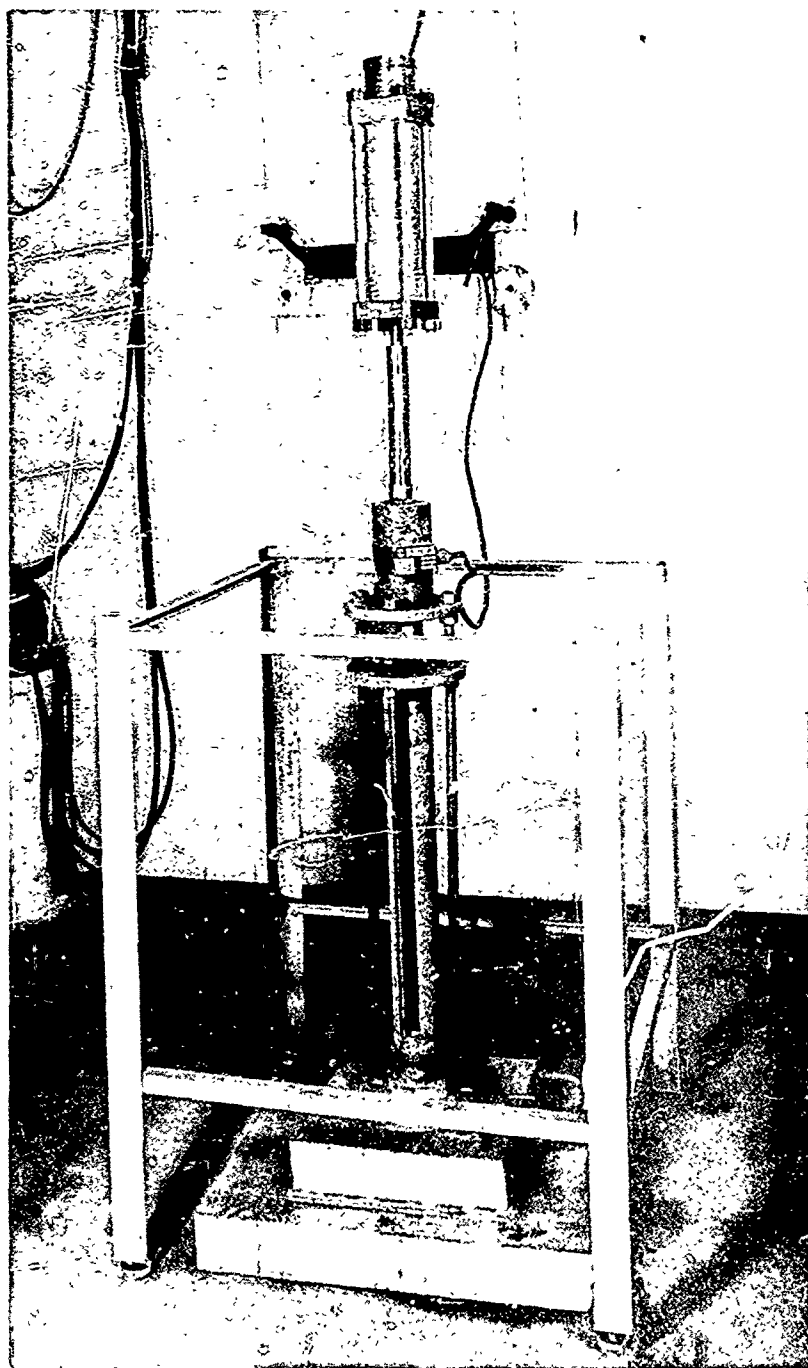


Figure 5. Test Motor Installed on Thrust Stand

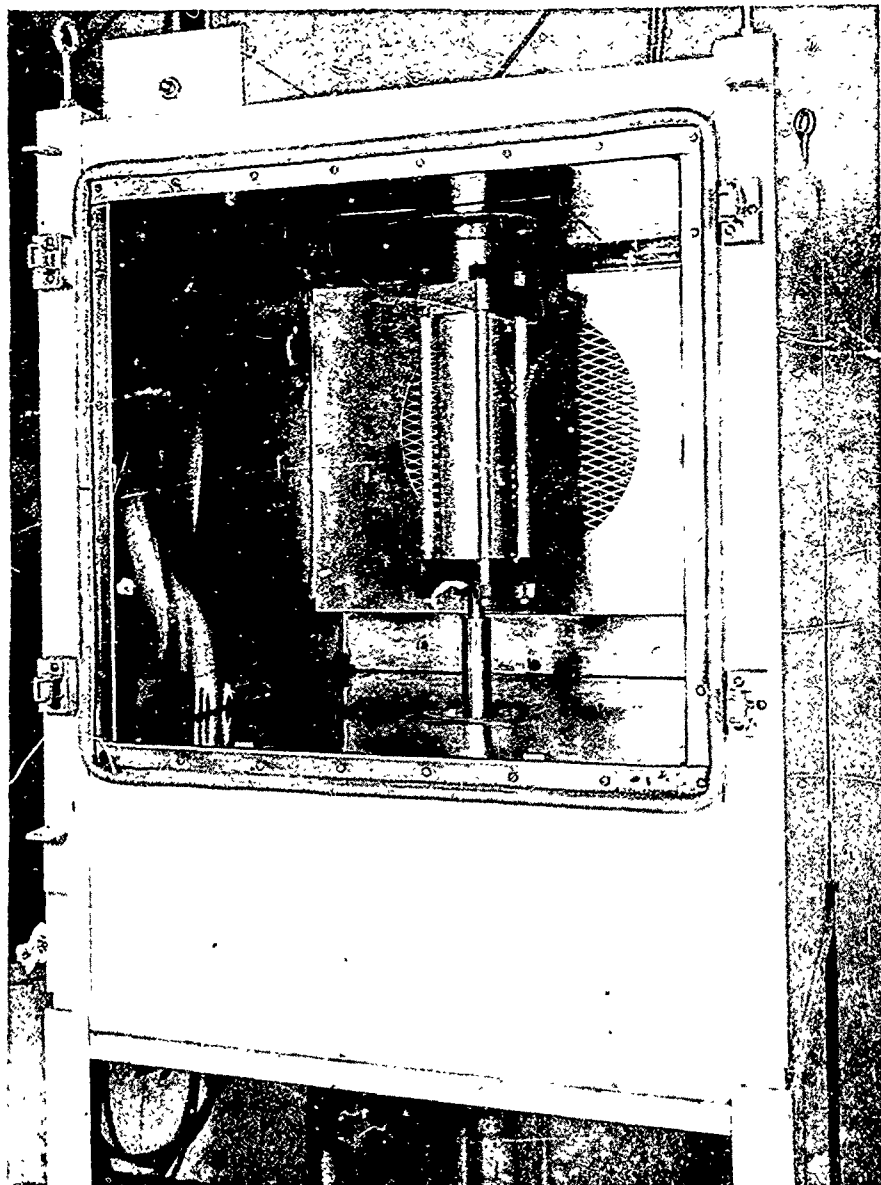


Figure 6. Test Motor with Conditioning Chamber

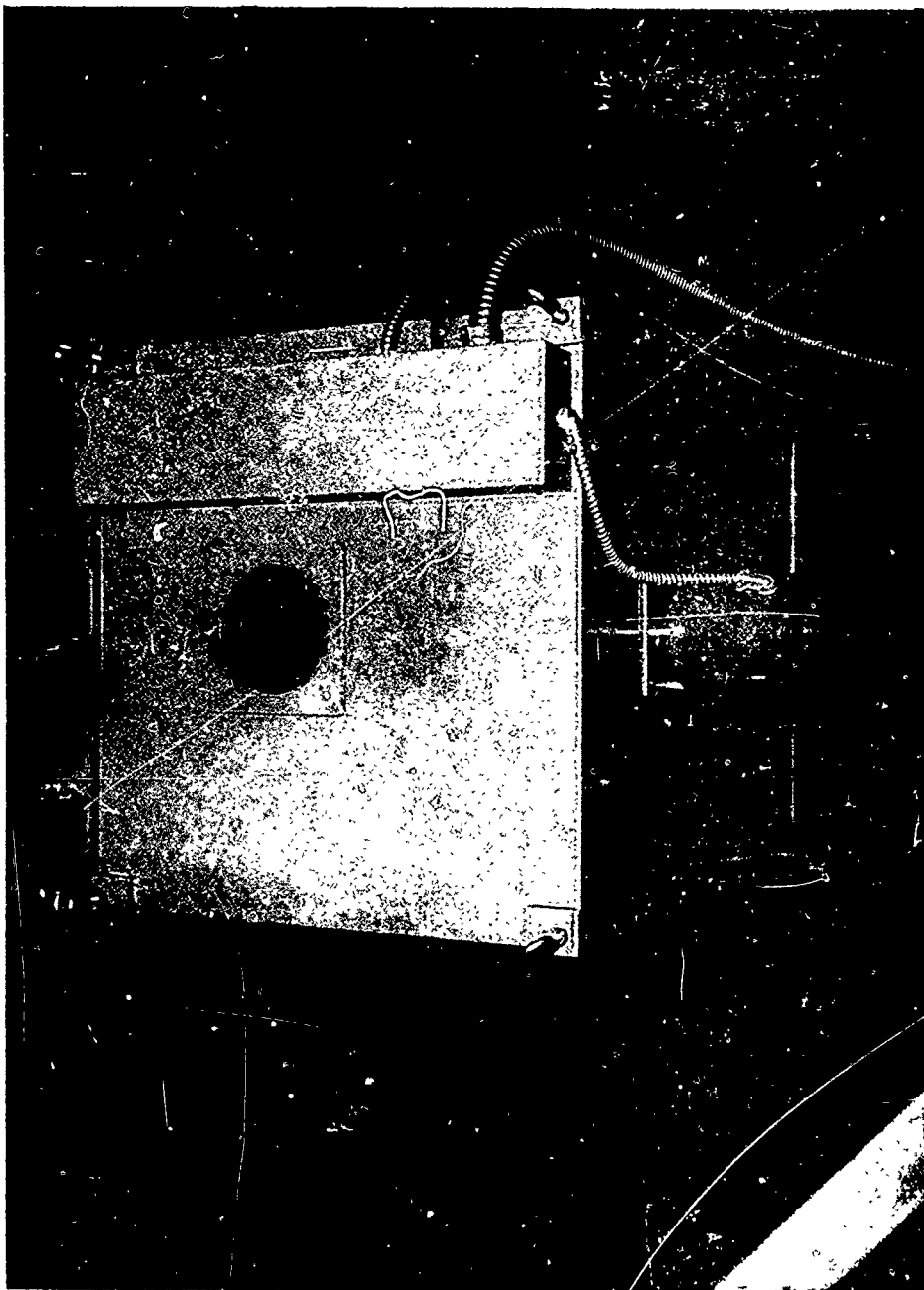


Figure 7. Test Motor in Conditioning Chamber, showing Top Port

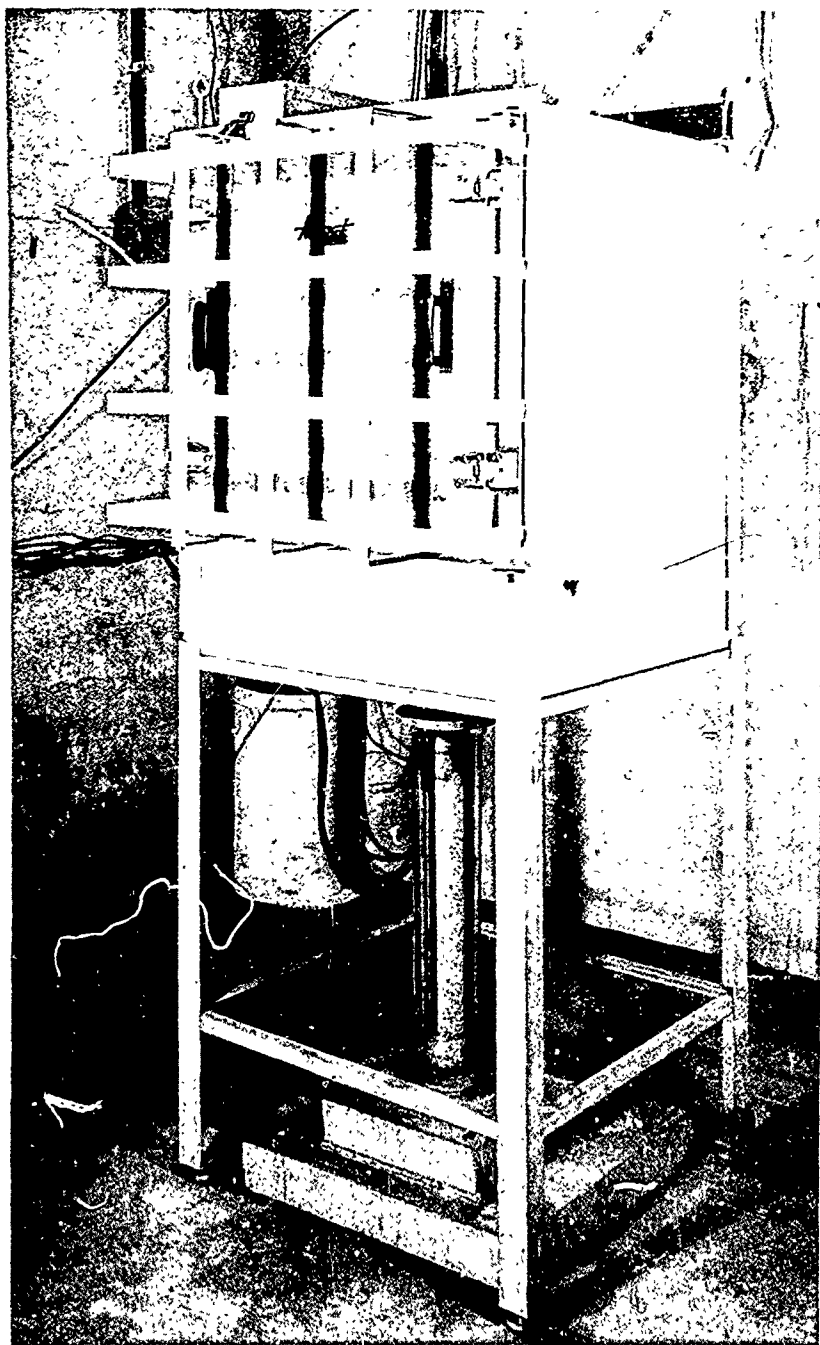


Figure 8. Conditioning Chamber, in Run Condition

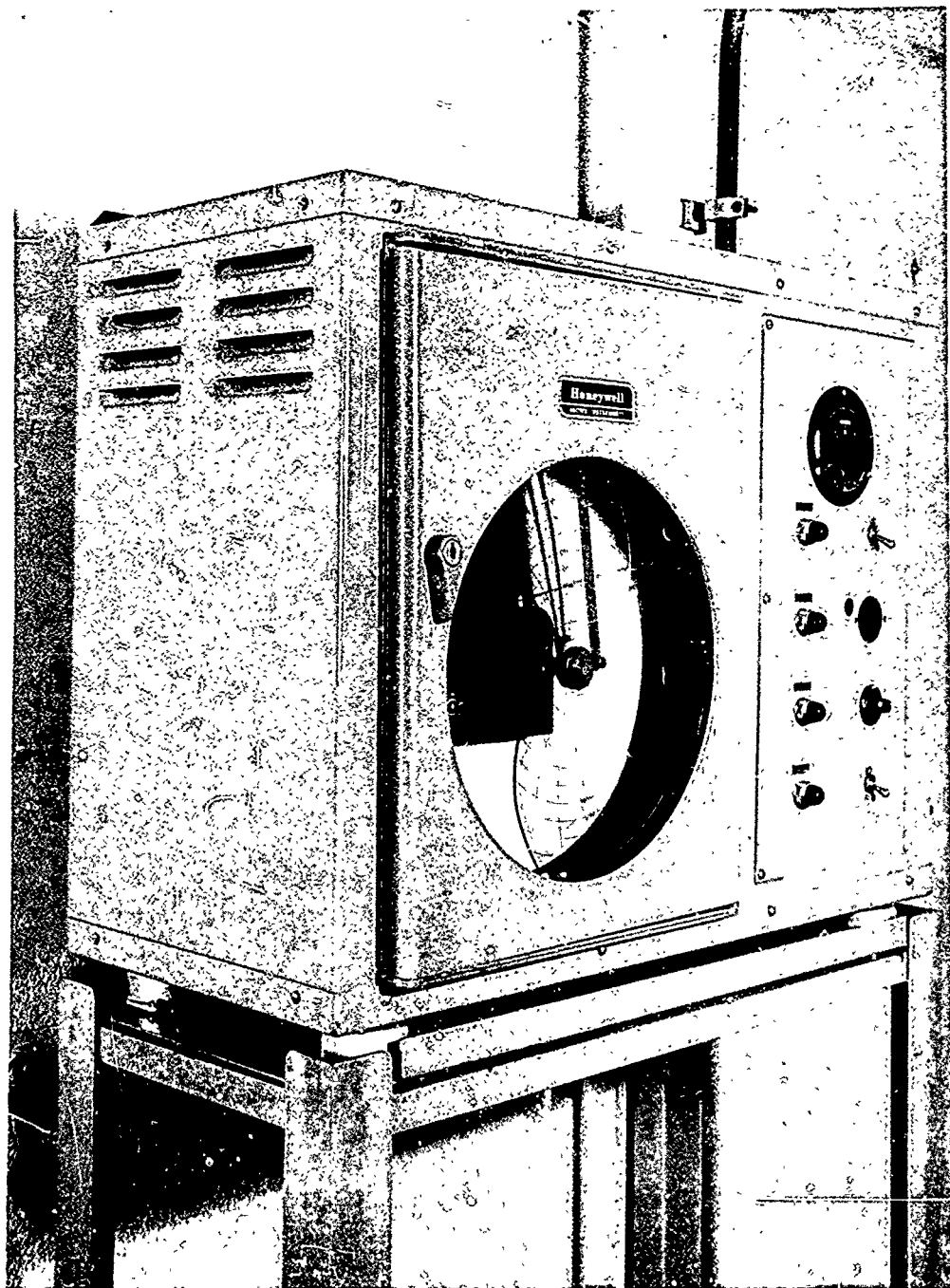


Figure 9. Programmer-Controller

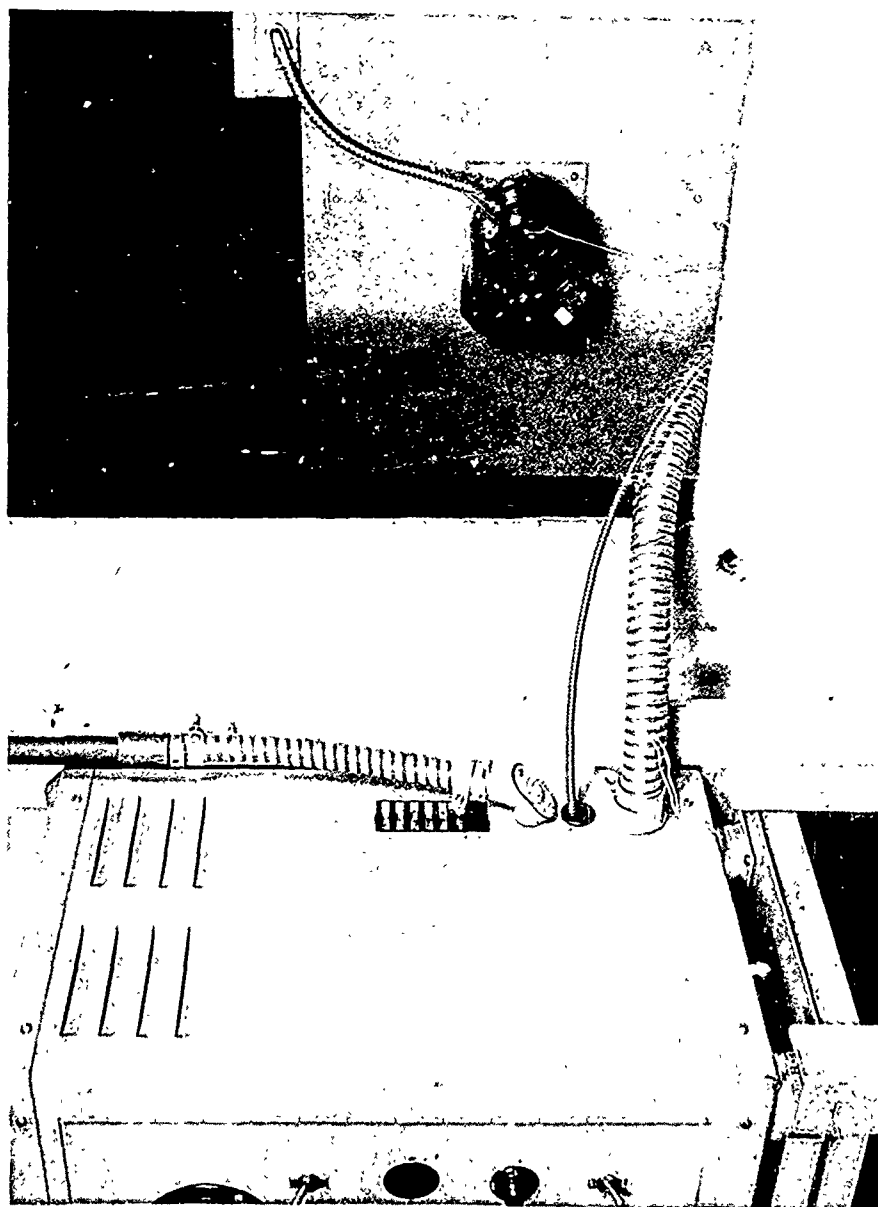


Figure 10. Aft End of Conditioning Chamber, viewed through Barricade

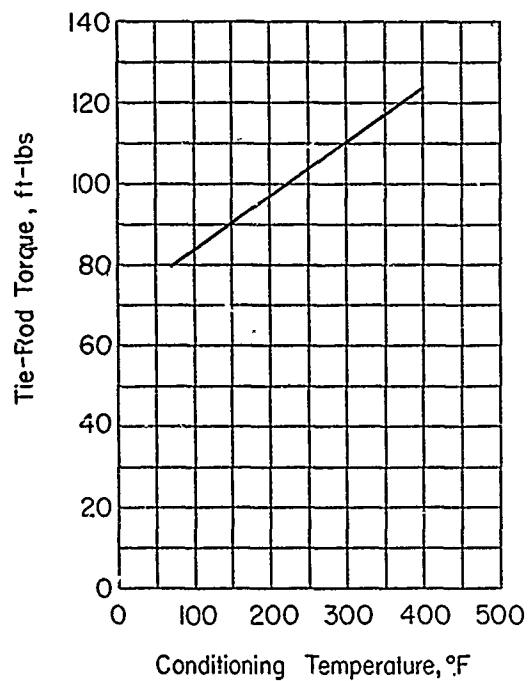


Figure 11. Tie Rod Torque vs Conditioning Temperature

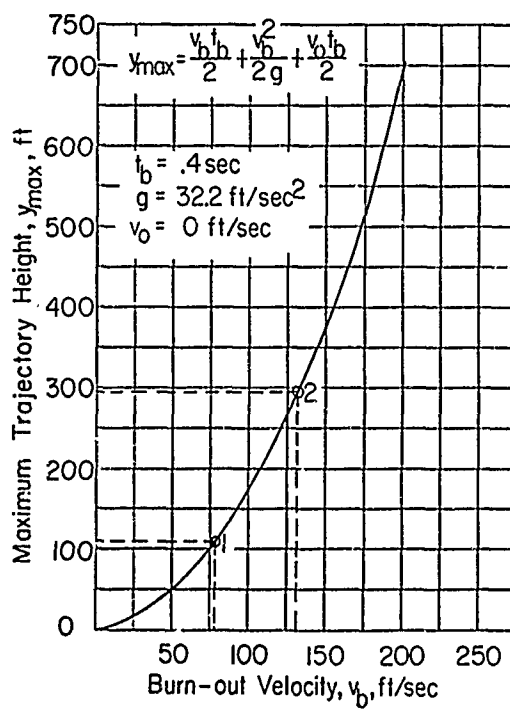


Figure 12. Peak Chamber Pressure vs Conditioning Temperature

The motor tube is made of stock 3-1/4 inch OD normalized 4130 alloy steel to reduce the fragmentation caused by a motor detonation. The nozzle is made of American high density graphite (AHDG), whose erosion rate is low. Igniter baskets are made of stainless steel. Various modes of central ignition can be used to suit the propellant. Traps are made of precision cast alloy steel and are designed to provide a constant port, the same size as the propellant port.

Grain design varies with the method of loading. The J factor is controlled to eliminate erosive burning as a factor in the data. The AK14 Mod 1 propellant is manufactured without restriction and is supported by the trap and resonance rod attached to the head. Case-bonded and extruded grains have the same center perforation as the typical escape rocket, but the length is 8 inches instead of 36 to 40 inches. Thus, any candidate propellant can be quickly scaled up to a full size grain and tried in a service type rocket motor.

TEST PROGRAM AND RESULTS

The test program was initiated with the AK14 Mod 1 propellant. It was fired at -65°, 70°, 200°, 250°, 300°, 350° and 400° F. Detailed data are shown in Table I and a summary of maximum pressure vs temperature is shown in Figure 12. The curve appears to fit a parabola; i. e., the maximum chamber pressure seems to be a parabolic function of conditioning temperature. At 70° F, the peak pressure is about 1000 psi, but at 400° F the pressure is about 4 times greater, or more than 4500 psi. This spread is unfavorable if the 20 g upper limit is imposed at 400° F. If 3600 lbf is equivalent to 20 g at 400° F, the following tabulation illustrates the large change of thrust.

Temperature (°F)	Max Thrust (lbf)	Equivalent Acceleration (g)
400	3600	20.0
67	950	5.3
-65	650	3.6

Although the thrust changes with temperature, the total impulse remains nearly constant. However, the burn time increases as the temperature decreases. If the escape must be accomplished in a minimum time and with a constant thrust, the cross-sectional area of the nozzle must be variable. This variation will be a function of temperature and the small throat area will be at low temperature.

TABLE I. Data for Rocket Motor Static Tests Using AK14 Mod I Grain and 0.790 inch ID Nozzle

TABLE I. Data for Rocket Motor Static Tests Using AK14 Mod I Grain and 0.790 inch ID Nozzle

Notes: Where grain weight is not recorded, average grain weight was used to compute specific impulse.
All grains were 714 in. long by 2.6 in. OD by 0.6 in. ID.
Throat exit diameter was 2.35 in.

CODE: CD - Coefficient of discharge.
CF - Coefficient of thrust.
Fm - Maximum thrust.
Fp - Specific impulse.
Isp - Total impulse.
Pdt - Integral of pressure with respect to time.
Pi - Final peak pressure.
Pm - Initial peak pressure.
Pn - Action time interval from 10 percent of maximum peak pressure on rise portion of pressure-time trace.
tb - Burn time interval from 10 percent of maximum peak pressure on rise portion of pressure-time trace to web burnout.
td - Ignition delay time interval from fire pulse to 10 percent of maximum peak pressure on rise portion of pressure-time trace.

Precoolant Test No.	Precoolant Material	Insulator Material	Conditioning Temp (°F)	Firing Temp (°F)	Pretest Throat Area (in. ²)	Post Firing Throat Dia (in.)	P1 (psi)	P2 (psi)	P3 (psi)	Tc (°F-avg)	Tsp (°F-avg)	Pdc (psi-avg)	CF	Qp × 10 ³ lb-sec	cd (sec)	tb (sec)	td (sec)	Remarks	
1-1	NR	BKNO ₂ 2R 14	Amb	57	0.7903	0.4906	300	1120	1120	950	245	335	1.50	10.00	0.038	0.345	0.372	1	
1-2	NR	BKNO ₂ 2L 20	Amb	62	0.7903	0.4906	120	1270	1270	920	235	335	1.45	9.95	0.030	0.333	0.372	1	
1-3	NR	BKNO ₂ 2K 20	Amb	65	0.7906	0.4908	1010	1190	1190	890	245	335	1.50	9.92	0.044	0.303	0.337	2	
1-4	NR	BKNO ₂ 2K 25	Amb	65	0.7904	0.4906	1170	1200	1190	870	250	340	1.50	9.83	0.016	0.310	0.343	2	
1-5	NR	BKNO ₂ 2K 20	Amb	67	0.7902	0.4904	980	1180	1180	900	250	340	1.50	9.83	0.049	0.317	0.344	2	
1-6	NR	BKNO ₂ 2K 20	200	17.5	0.7900	0.4901	1540	1540	1540	650	245	340	1.45	9.87	0.044	0.214	0.231	1	
1-7	NR	BKNO ₂ 2K 20	18.5	0.7900	0.4901	0.7900	440	870	870	1350	245	340	1.45	9.20	0.039	0.425	0.453	1	
1-8	NR	BKNO ₂ 2K 20	200	4.5	0.7891	0.4889	1410	1830	1830	1350	265	360	1.50	9.37	0.012	0.214	0.239	1	
1-9	NR	BKNO ₂ 2K 20	200	4	0.7925	0.4930	0.7960	1550	1850	1860	1210	130	345	1.25	9.55	0.020	0.245	0.270	1
1-10	NR	BKNO ₂ 2K 20	200	3.5	0.7960	0.4976	0.7940	1530	1860	1870	1350	375	1.45	8.84	0.188	0.230	0.250	1	
1-11	NR	BKNO ₂ 2K 20	250	4	0.7900	0.4902	0.7960	1700	2420	2330	1730	365	360	1.50	9.18	0.005	0.170	0.200	2
1-12	NR	BKNO ₂ 2K 20	300	4	0.7890	0.4889	0.802	1900	2680	2660	1930	375	360	1.55	9.35	0.023	0.150	0.175	2
1-13	NR	BKNO ₂ 2K 20	350	4	0.7830	0.4815	0.806	3170	2720	2250	250	355	1.45	9.48	0.018	0.130	0.150	2	
1-14	NR	BKNO ₂ 2K 20	400	4	0.7940	0.4951	0.806	2460	4530	4500	3600	355	1.45	9.48	0.023	0.130	0.150	2	

Remarks: 1. Ignition poor; burning good.
2. Ignition and burning good.
3. Ignition good. Motor dumped from overpressure.

The next test series (Table II) of AK14 Mod 1 was fired with an 0.850 inch ID nozzle in place of the 0.790 inch ID nozzle. The firing temperatures were -100°, -65°, 70°, 200°, 300°, and 400° F, and they coincide with the temperatures fired with the smaller nozzle. Cycling tests were initiated between -100° and +400° F for the second portion of the series. The soak time at each temperature was 4 hours in a 12-hour period, with the remainder of the time used for heating and cooling. However, the firing temperature of the cycled rounds was changed to 70° F so that a change in propellant performance could be more easily seen. As the cycling time increased from 24 to 108 hours, the propellant performed almost without change. If there was a change, the round-to-round variation masked it. After nine times at 400° F (a total of 36 hours), the I_{sp} remained near 160 lbf-sec/lbm ($\rho I_{sp} \approx 10.7$ lbf-sec/in.³).

Limited testing was conducted with the PL6670 propellant (Table III). Ceramic nozzle exit cones were used after the second test because of the severe erosion in the exit cone area. (See Figures 13 through 16.) The next rounds were conditioned at 400° F to check high temperature resistance after four hours. However, the performance was poor, in contradiction of the good resistance predicted by the differential thermal analysis (DTA). (See Figure 17 and the Appendix.) Additional tests should be made through the temperature range before judging the stability of PL6670. The density impulse ($\rho I_{sp} \approx 13$ lbf-sec/in.³) of this propellant is better than for AK14 Mod 1.

Heavy web KP-Hycar propellant was made in pilot lots at the Naval Ordnance Station (NOS), Indian Head, Md. However, no propellant has been made for the tie rod test motor. (The work at NOS will be described in a Technical Note to be published under separate cover.)

TABLE II. Data for Rocket Motor Static Tests Using AK14 Mod I Grain and 0.850 inch ID Nozzle

TABLE II. Data for Rocket Motor Static Tests Using AK14 Mod 1 Grain and 0.850 Inch ID Nozzle

Note: Throat exit diameter was 2.35 in.

CODE	CD	Coefficient of discharge.
CF		Coefficient of thrust.
F _m		Maximum thrust.
I _{sp}		Specific impulse.
It		Total impulse
pt		Integral of pressure with respect to time.

- Final peak pressure.
- Initial peak pressure
- Maximum peak pressure
- Action time interval from 10 percent of maximum pressure to final peak pressure.
- Burn time interval from 10 percent of maximum pressure to final peak pressure.
- Ignition delay time interval from fire pulse to initial peak pressure.

Test Height (in)	Recoilant Weight (lb)	Inertial Material	Weight (lb)	Conditional Temp (°F)	Firing Time (μs)	Minimum Thrust Along Axis (lbf)	Post Firing Thrust Dia (in)	P ₁ (psia)	P ₂ (psia)	P ₃ (psia)	P ₄ (psia)	P ₅ (lbf)	T _c (100°F/in)	I _{sp} (lbf·sec/lbf)	P _{de} (psia/lbf)	C _p	Q ₀ × 10 ³ 100-msec	T _d (msec)	V ₀ (msec)	C _a (sec)	Remarks																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																										
																						Material	Temp (°F)	Thrust (lbf)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)	Temp (°F)

the Nozzle exits during disassembly: repaired, using allbond.

Grain quenched. Weight of grain after test, 1.46 lb.

Conditioning time cut from planned 60 hours to 48 hours due to failure of temperature conditioning ϵ /stem.

Conditioning time cut from planned 12 hours to 31 hours due to failure of temperature conditioning system.

•

1. Igalton and burning good.
2. Igalton poor: burning good.

3. Ignition and burning poor.

5. Delivery failure. CO₂ exhausted. Test terminated at 42 hours.

6. Final 4 hour cold cycle not completed to meat range schedule.

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TABLE III. Data for Rocket Motor Static Tests Using PL6670 Grain

TABLE III. Data for Rocket Motor Static Tests Using PL6670 Grain

Note. Throat exit diameter was 2.35 in.

CODE -
 CD - Coefficient of discharge.
 CF - Coefficient of thrust.
 F_{max} - Maximum thrust.
 I_{sp} - Specific impulse.
 I_t - Total impulse.
 P_{dt} - Integral of pressure with respect to time.
 P₀ - Initial peak pressure.
 P_m - Maximum peak pressure.
 P_a - Action time interval from 10 percent of maximum peak pressure on rise portion of pressure-time trace to 10 percent of maximum peak pressure on decay portion of pressure-time trace.
 t_b - Burn time interval from 10 percent of maximum peak pressure on rise portion of pressure-time trace to web burnout.
 t_d - Ignition delay time interval from fire pulse to 10 percent of maximum peak pressure on rise portion of pressure-time trace.

Propellant Weight (lb)	Igniter Material	Igniter Weight (g)	Conditioning Time (hr)	Firing Time (μ sec)	Post-Firing Time (μ sec)	Post-Firing Thrust Data (lb)	P_0 (psi)	P_d (psi)	F_m (lb)	I_t (lb-sec)	I_{sp} (lb-sec/lbm)	C_D (μ sec)	t_b (sec)	t_d (sec)	Remarks	
2-1	PL6085	15	70	NA	70	N/C	110	1090	1090	800	530	1.44	9.14	0.031	0.88	1
2-2	PL6085	15	70	NA	70	N/C	180	1230	1830	1040	550	1.59	9.67	0.031	0.84	1
2-3a	PL6085	15	70	NA	70	N/C	190	800	830	690	490	1.82	7.93	0.120	0.93	1
2-2b	PL6085	15	400	4	70	N/C	2350	-	-	-	-	-	-	-	-	2
2-2c	PL6085	15	400	4	70	N/C	2350	-	-	-	-	-	-	-	-	3

Remark: 1. Ignition and burning good.
 2. Ignition poor, no burning.
 3. Ignition and burning poor.

a Ceramic nozzle used in this and subsequent tests because of severe erosion in exit cone area.
 b Grain failed to ignite on first attempt. Additional igniter placed in primer tube. Additional igniter caused overignition, motor failed.
 c Firing conducted before motor reached ambient temperature after conditioning at 400° F. estimated about 100° F. overignition, grain burned at low pressure.



Figure 13. Nozzle Exit after Firing

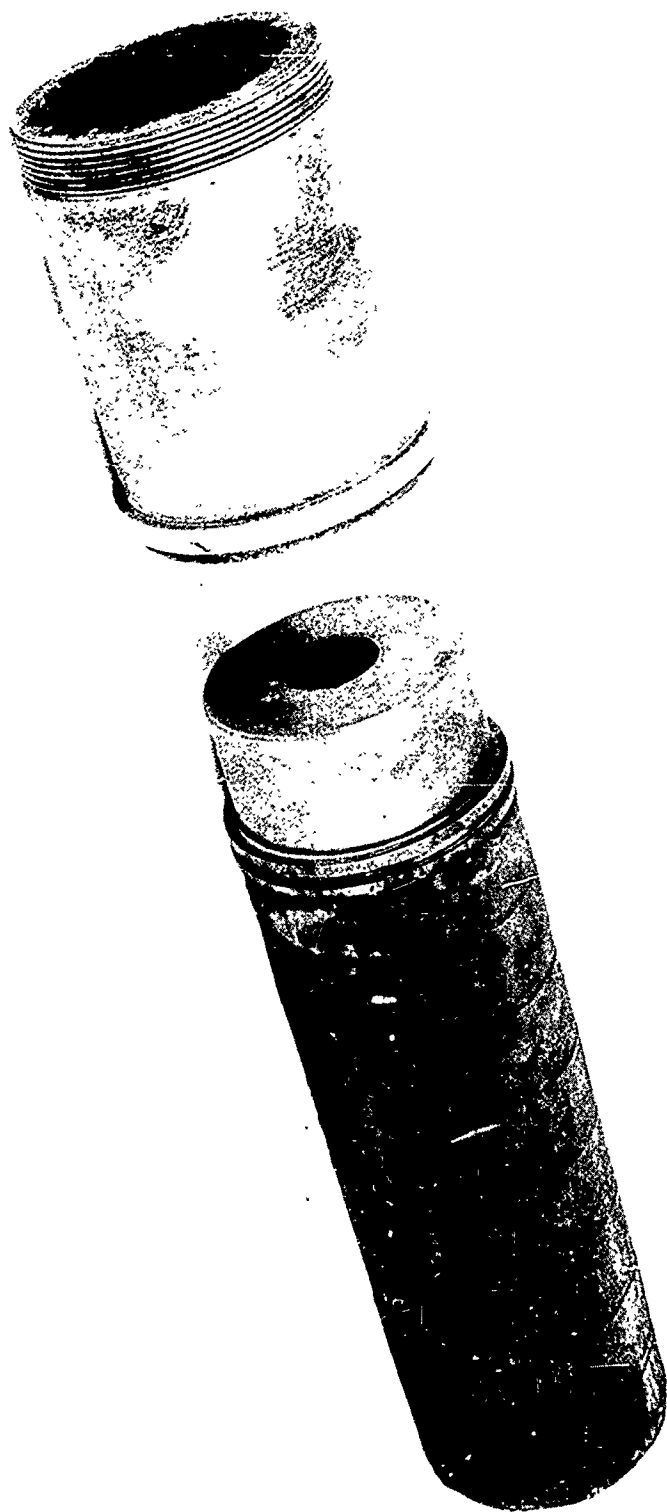


Figure 14. Nozzle, Carbon Insert, and Inhibitor after Firing

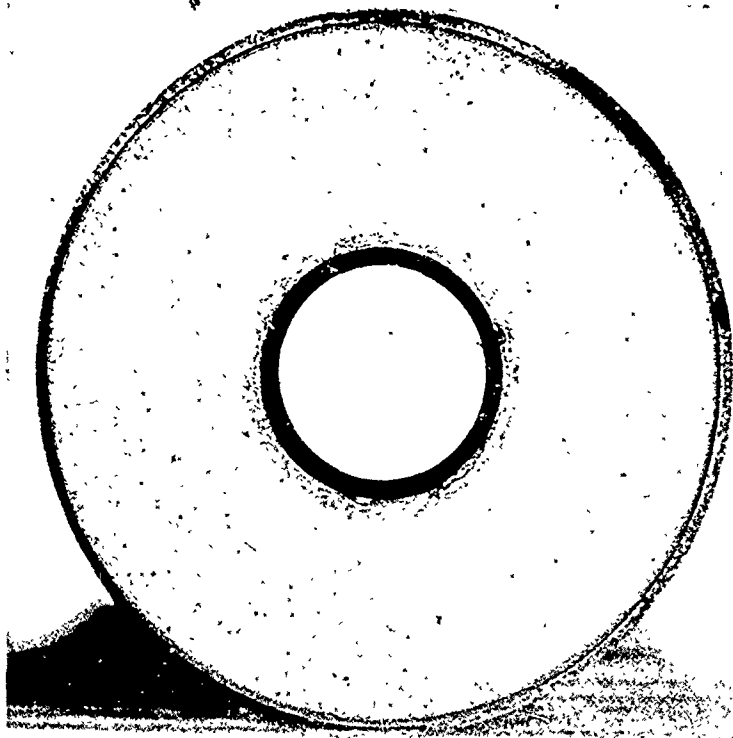


Figure 15. Carbon Insert Entrance after Firing

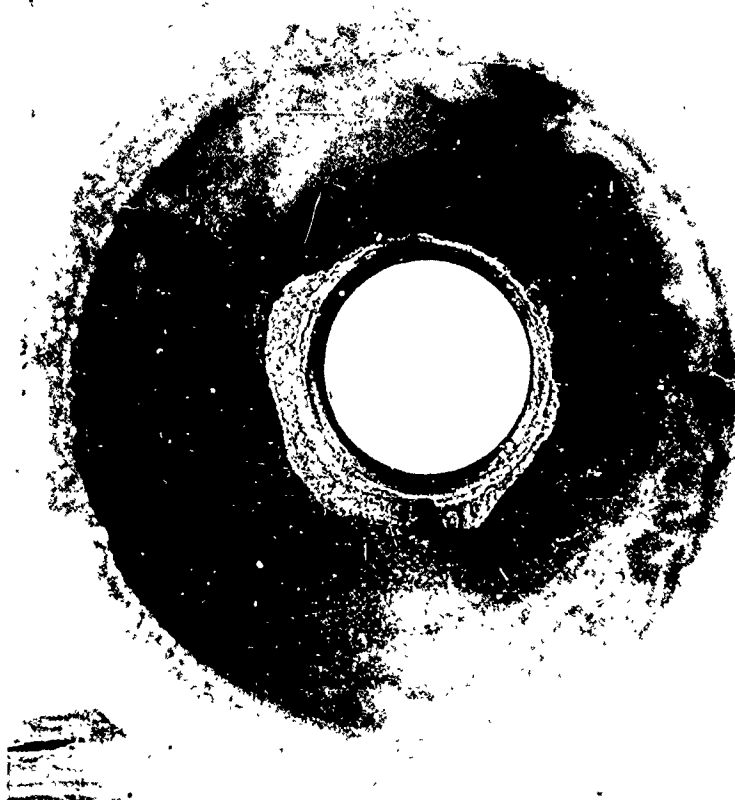


Figure 16. Nozzle Exit and Carbon Insert after Firing

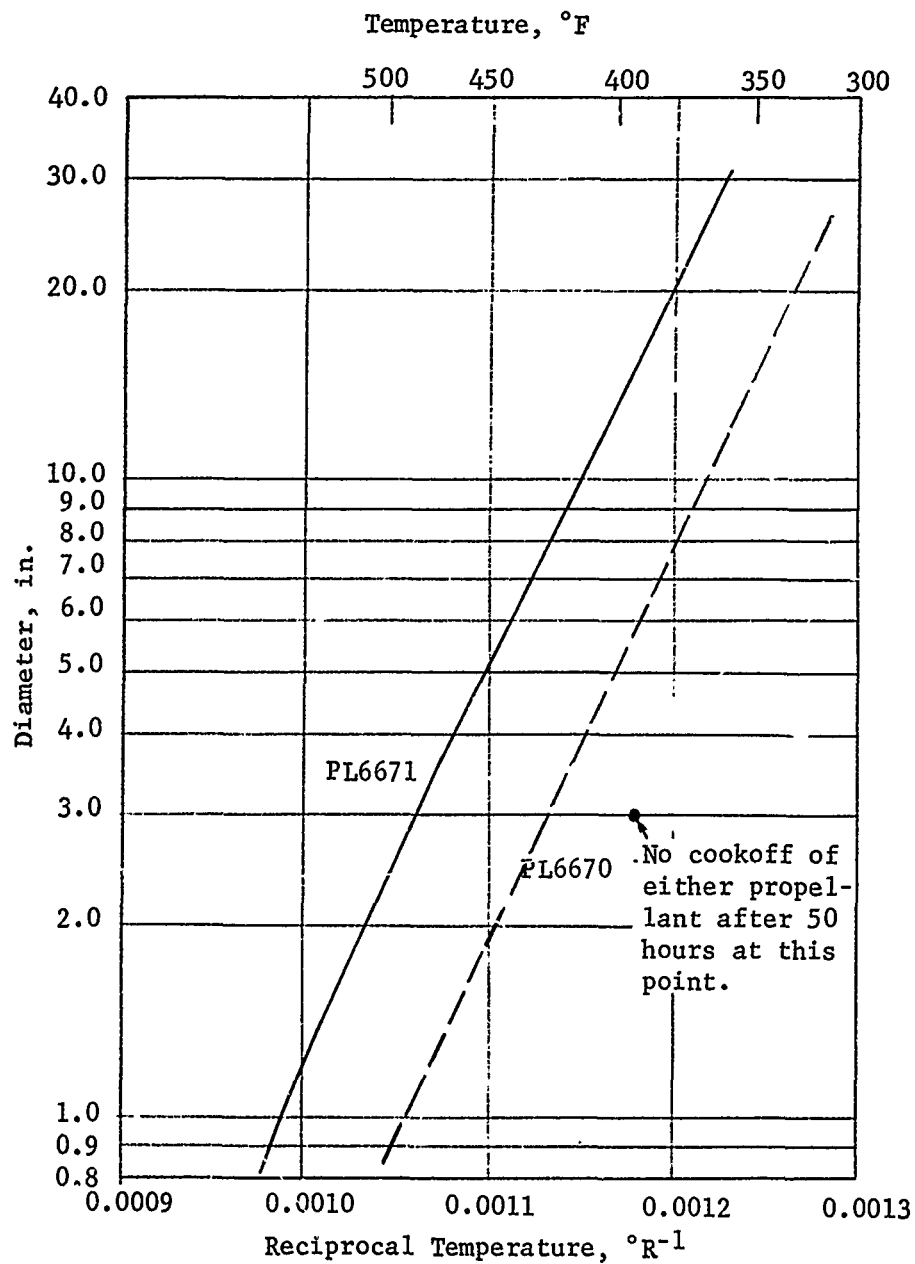


Figure 17. Critical Oven Temperatures (predicted from DTA) for Solid Rod as a Function of Billet Diameter for PL6670 and PL6671

(Reprinted from Reference 7.)

CONCLUSIONS

The installation and the shakedown of the test equipment have proceeded to a satisfactory point. Most of the problems of technique appear to have been solved.

Preliminary testing shows that AK14 Mod 1 propellant has a very satisfactory thermal resistance for this application but, as expected, has a low density impulse.

PL6670 appears to have increased density impulse as desired, but testing has not proceeded far enough to evaluate this propellant at elevated temperatures.

Although these propellants appear to meet the established criteria, they exhibit the temperature dependency and the high burning rate exponent typical of KP oxidized propellants.

Future work should be directed to lowering the burning rate exponent, reducing the temperature dependency of performance, and developing propellants with mesa or plateau characteristics.

APPENDIX

PL6670 PROPELLANT

PL6670 Propellant Data

Data were obtained on PL6670 propellant fired in 2 inch Gimlet motors at U. S. Naval Weapons Center, China Lake, Calif. These data are presented in Table IV and quality control data are presented in Table V.

Thermal Decomposition Studies*

A thermal decomposition study was performed on PL6670 and PL6671 propellants, particularly at temperatures near 400° F. The methods of thermal analysis employed were differential thermal analysis (DTA) and isothermal analysis.

In the DTA studies, thermal patterns of each solid propellant were determined on sample sizes ranging from 20 to 30 milligrams. On each propellant, thermal patterns were studied for endothermic and exothermic peaks with respect to temperature at a given heating rate. The onset temperature to the first exothermic peak was noted since this indicates the first measurable evidence of the thermal decomposition of the propellant sample.

The activation energy (E) and frequency factor (A) were also determined for the exothermic peak by the variable heating rate and computed by a high speed digital computer. This method consists of a plot of the DTA data on each exotherm as log-heating rate over the absolute temperature. From this type of graph, the activation energy calculations were made based on the equation

$$\frac{d (\log \Phi/T^2)}{d (1/T)} = -\frac{E}{R} \quad (1)$$

where

Φ = heating rate, °C/min
T = absolute temperature of peak maximum
R = gas constant.

*J. M. Pakalak, Jr., "Thermal Decomposition Studies," U.S. Naval Weapons Center, Interoffice Memorandum for Record (Reg. 4532-19), 30 October 1964

TABLE V. Quality Control Data on PL6670 Propellant Batches
(from 0.21 in. diameter strands)

				Quality Control Data for Mix No.					
				<u>2878</u>	<u>2997</u>	<u>2998</u>	<u>2999</u>	<u>3000</u>	<u>3001</u>
CODE:	r_b	- Burning rate (in./sec)							
	p	- Pressure (psi)							
	ΔH_{ex}	- Heat of explosion (cal/g)							
r_b/p				0.488/340	0.658/335	0.670/330	0.704/335	0.606/335	0.641/330
				0.645/540	0.790/532	0.763/533	0.870/540	0.698/532	1.150/538
				0.719/725	0.990/735	0.826/735	0.909/740	0.840/735	0.909/740
				0.834/1038	0.910/1045	1.002/1035	1.042/1060	0.939/1040	1.067/1036
				1.042/1540	1.000/1555	1.923/1550	1.266/1555	1.020/1540	1.219/1540
				1.047/2025	1.852/2065	2.150/2070	1.481/2073	2.000/2070	1.869/2038
ΔH_{ex}				1.471/3083	2.502/3082	1.274/3075	1.742/3075	1.434/3068	1.419/3055
				1.818/4150	1.786/4075	2.632/4125	2.941/4125	2.273/4090	2.564/4080
Density (g/cc)				1762	1751	1753	1748	1762	
				2.2797	2.2772	2.3031	2.3081	2.2967	

Once the activation energy (E) value is determined, the frequency factor (A) can be calculated from the equation

$$A = e^{E/RT} \left[\frac{E \Phi}{RT^2} \right] \quad (2)$$

Then the specific rate constant, k, can be determined at selected temperatures via the Arrhenius equation

$$k = Ae^{-E/RT} \quad (3)$$

Thermograms of propellant PL6670, which were determined by DTA on an average sample size of about 25 mg, are shown in Figures 18 through 25, in order of increasing heating rate. The endothermic peak at 585° to 590° F in these thermal patterns is the transition temperature for potassium perchlorate. There are several exothermic peaks that occurred after the endotherm, but only the first two or three were used in the kinetic study. The onset temperature to these exotherms could be detected in the region from 500° F up to the starting of the exotherm for the potassium perchlorate transition.

DTA data are plotted in Figure 26 where the slope of the curve determines activation energy via Equation 1. The frequency factor and specific rate constant were evaluated via Equations 2 and 3, respectively. The activation energy, frequency factor, and the specific rate constant are given in Table VI.

Thermal patterns of propellant PL6671 were analyzed in the same manner as PL6670 and are given in Figures No. 27 through 32. The kinetic data are given in Table VII, and the plot for determining the activation energy in Figure 33. The main differences between these two propellants can be seen in the kinetic data.

The data from the DTA study are also used in predicting the critical temperature of a propellant of a given geometry and size. The critical temperature (T_m) is defined as the maximum surface temperature (T_1) that will allow a steady-state temperature distribution in a mass of material such as a propellant grain. The resulting equation for this condition is

$$T_m = \frac{E}{2.303 R \log \left[\frac{\rho a^2 QAE}{\lambda RT_1^2 \delta} \right]} \quad (4)$$

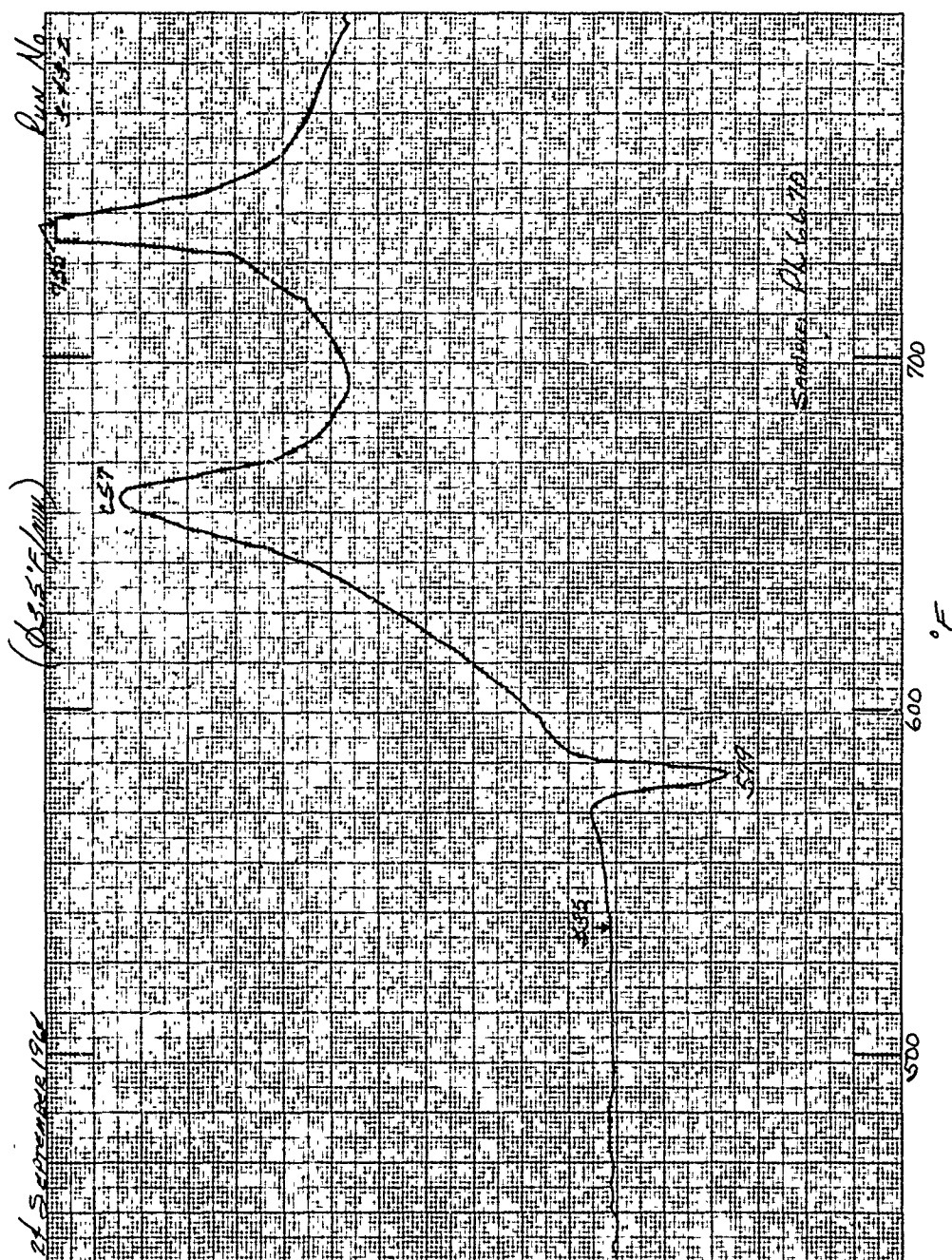
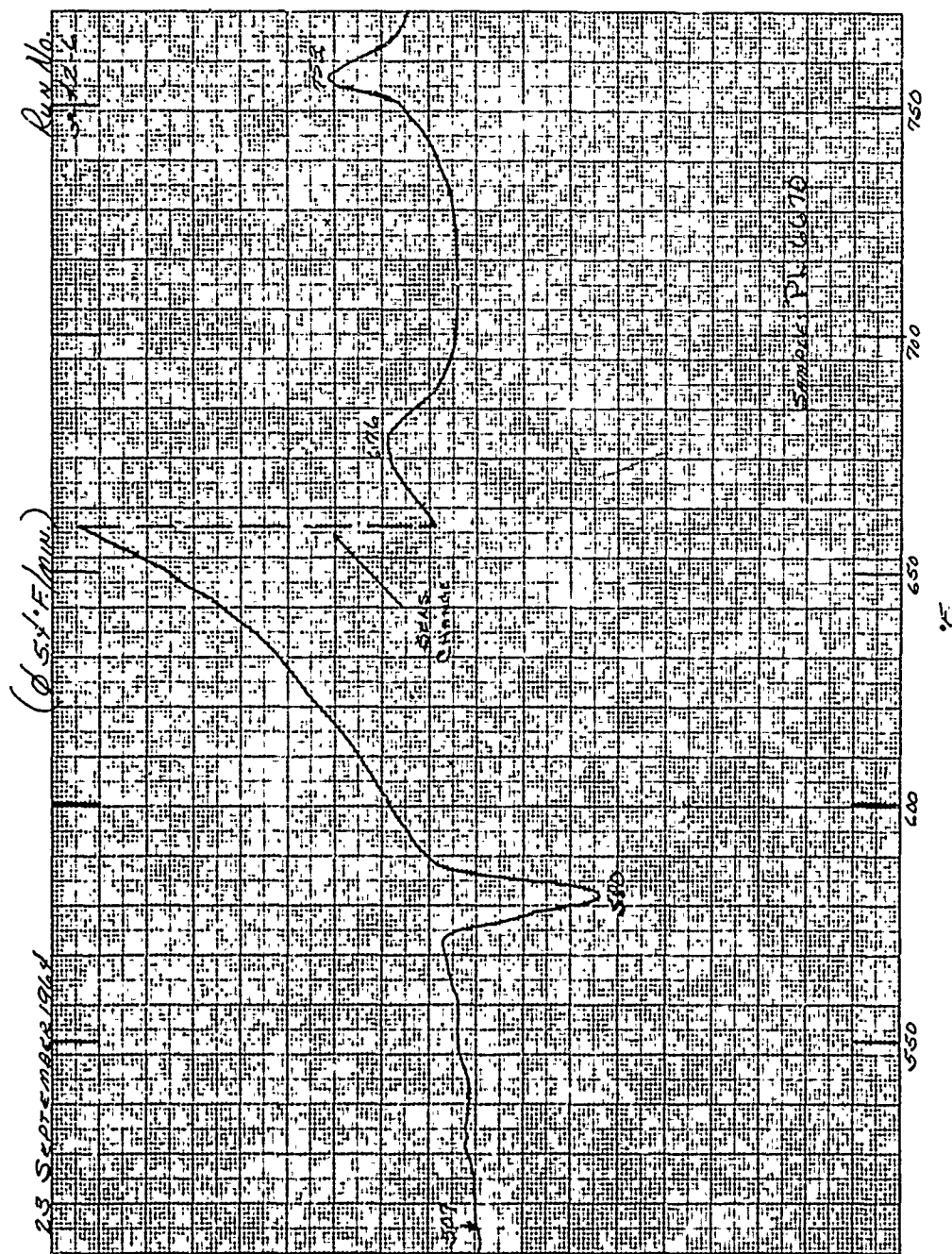


Figure 18. Thermogram, PL6670; $\phi = 3.5$ °F/min



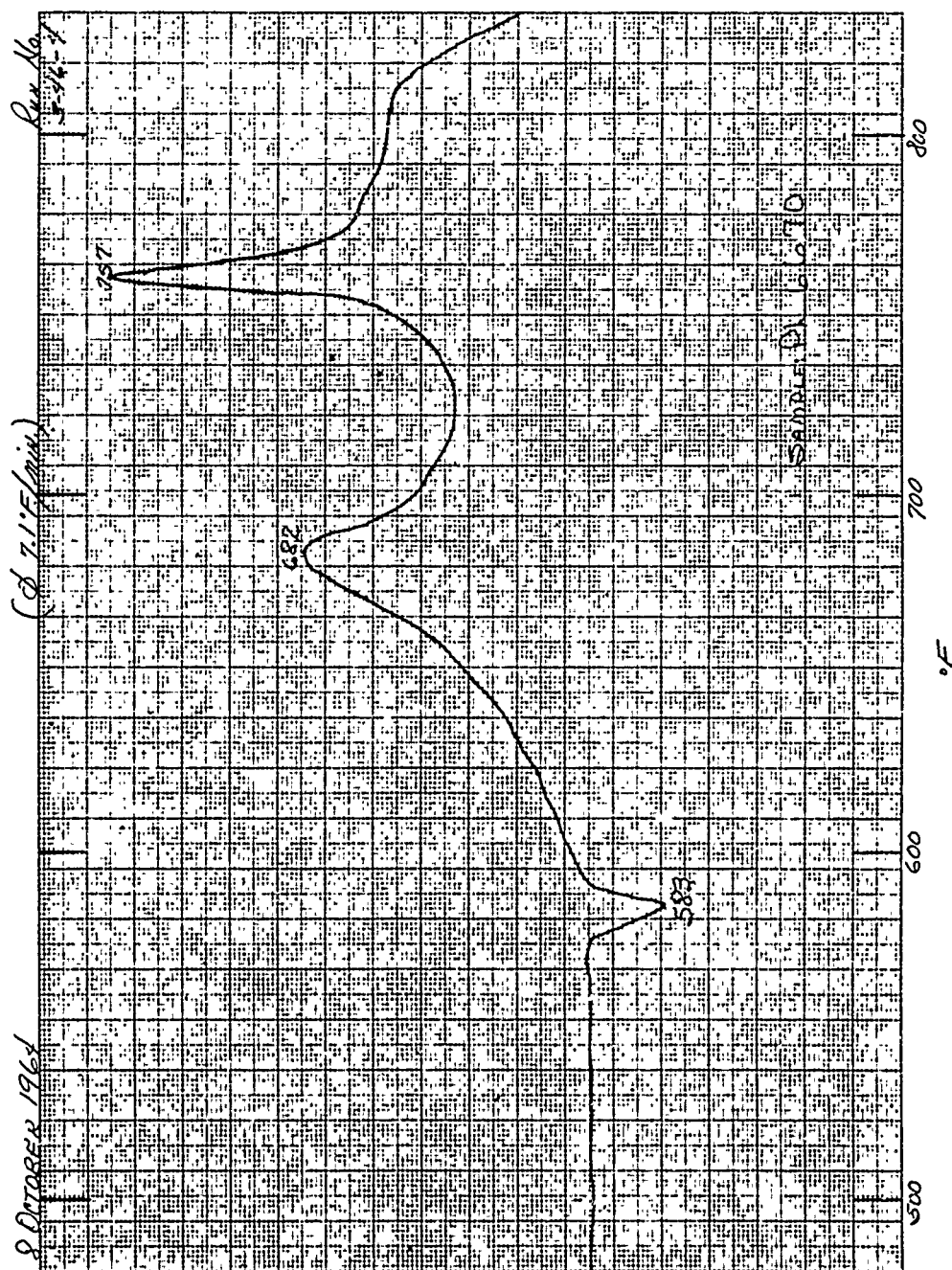


Figure 20. Thermogram, PL6670; $\Phi = 7.1$ °F/min

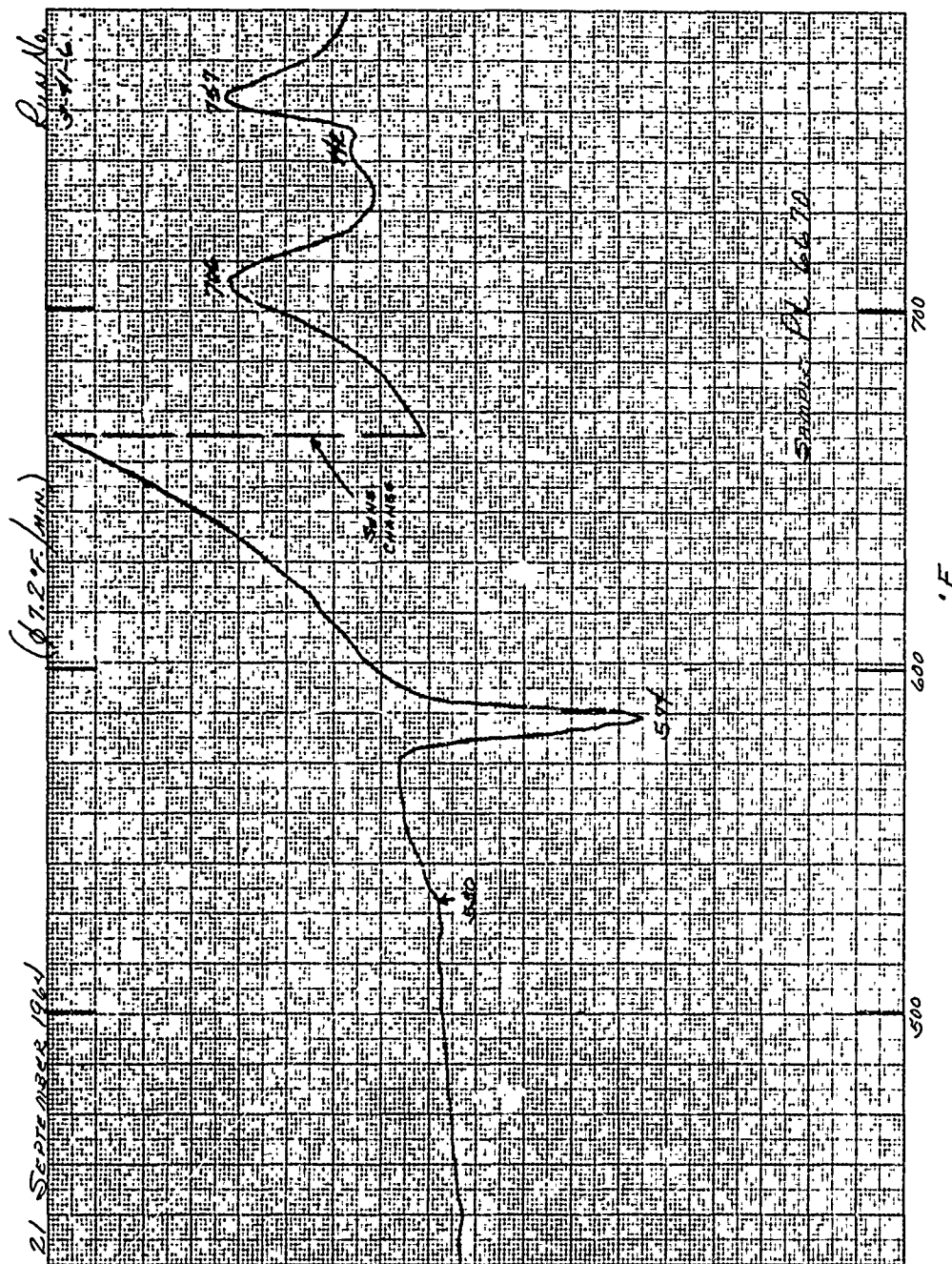


Figure 21. Thermogram, PL6670; $\Phi = 7.2$ °F/min.

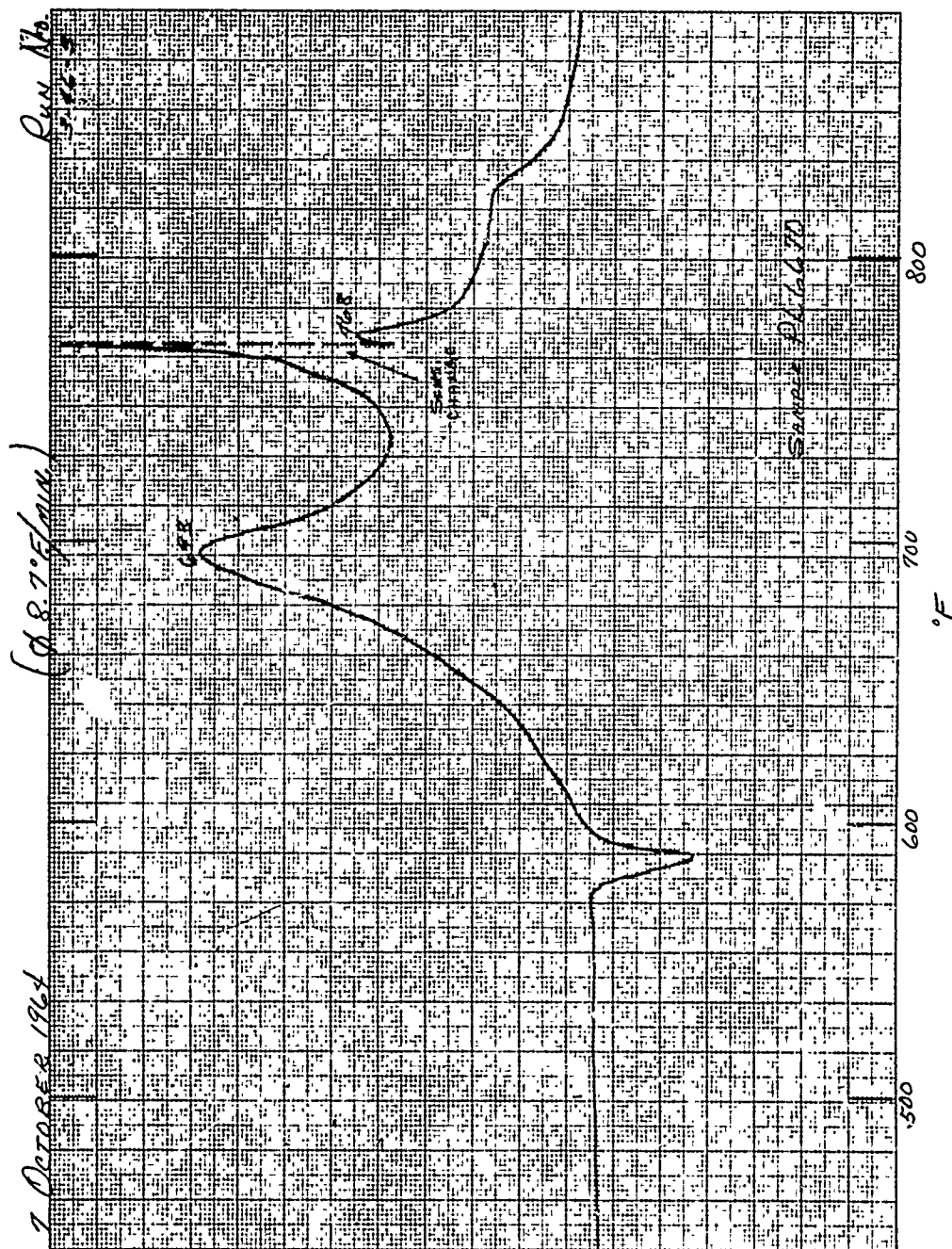


Figure 22. Thermogram, PL6670; $\Phi = 8.7$ °F/min

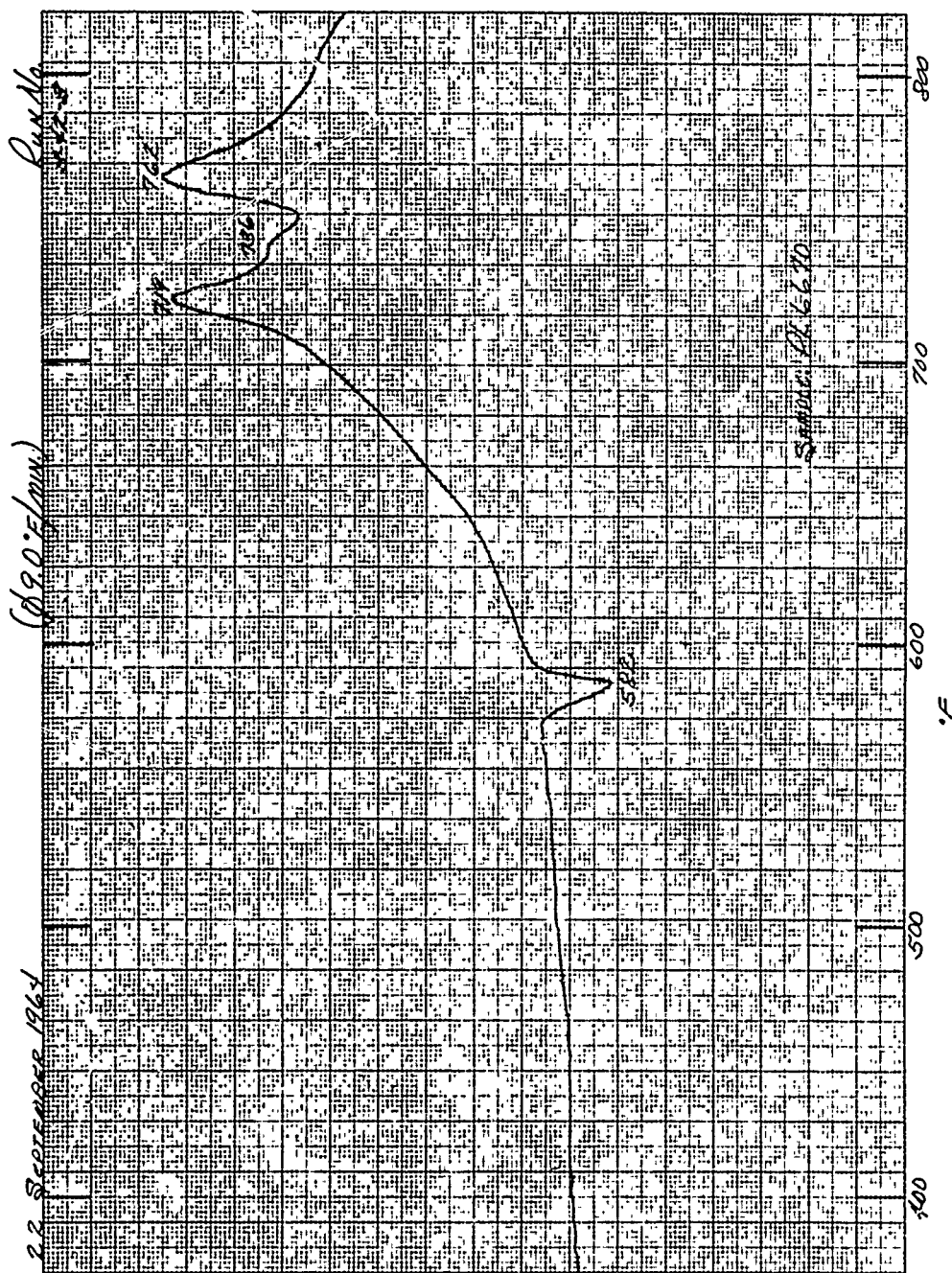


Figure 23. Thermogram, PL6670; $\Phi = 9.0$ °F/min

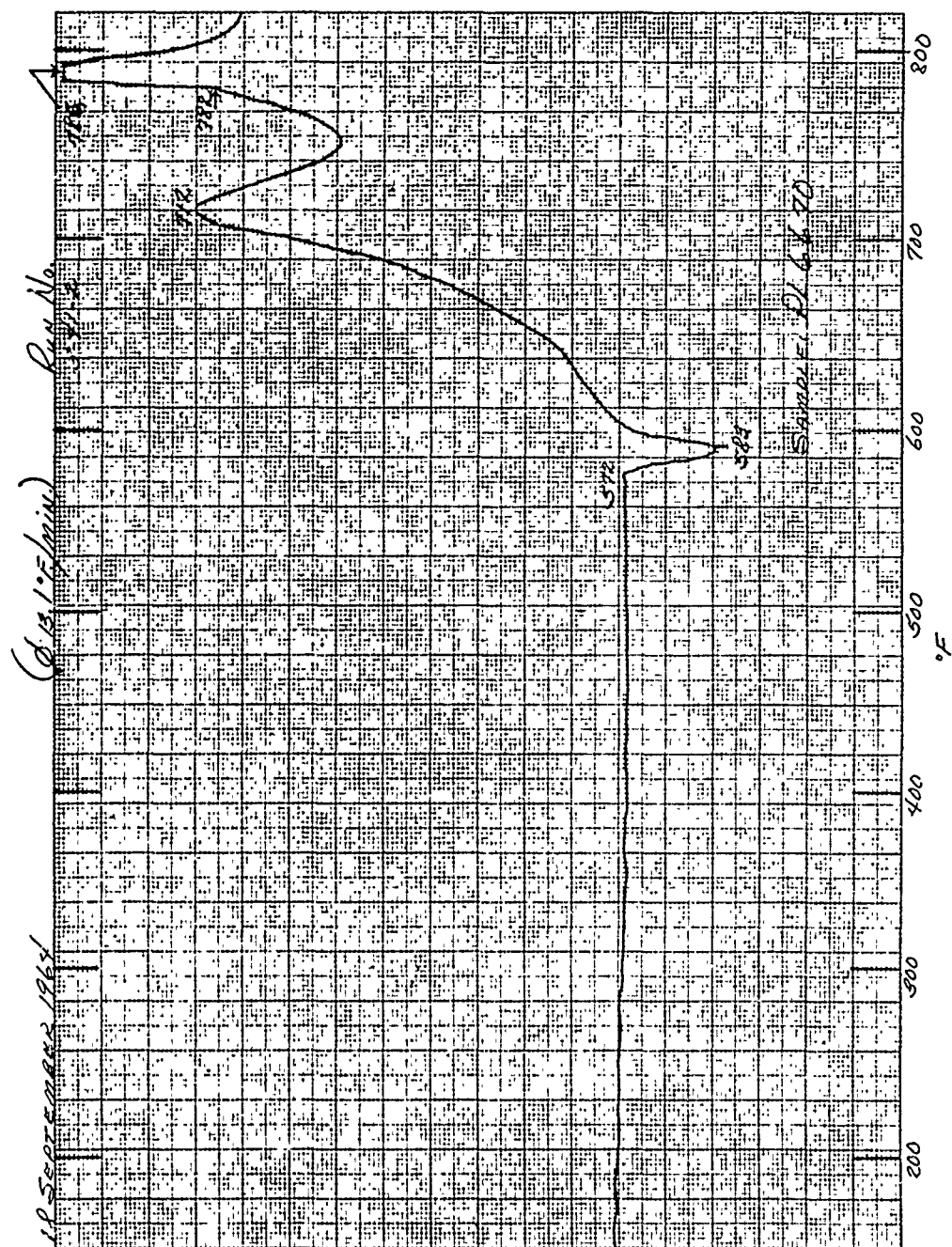


Figure 24. Thermogram, PL6670; $\Phi = 13.1$ °F/min

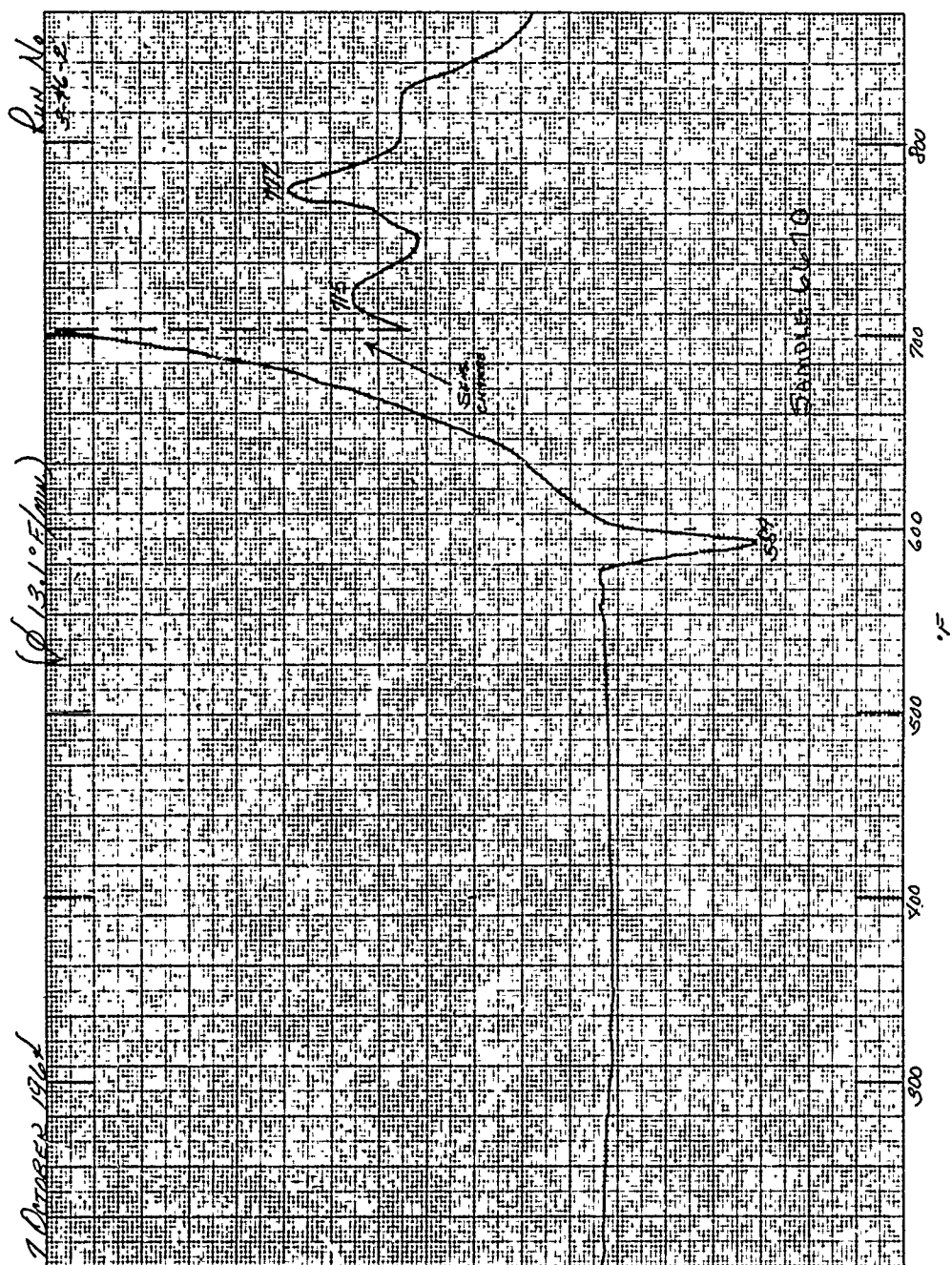


Figure 25. Thermogram, PL6670; $\Phi = 13.1$ °F/min

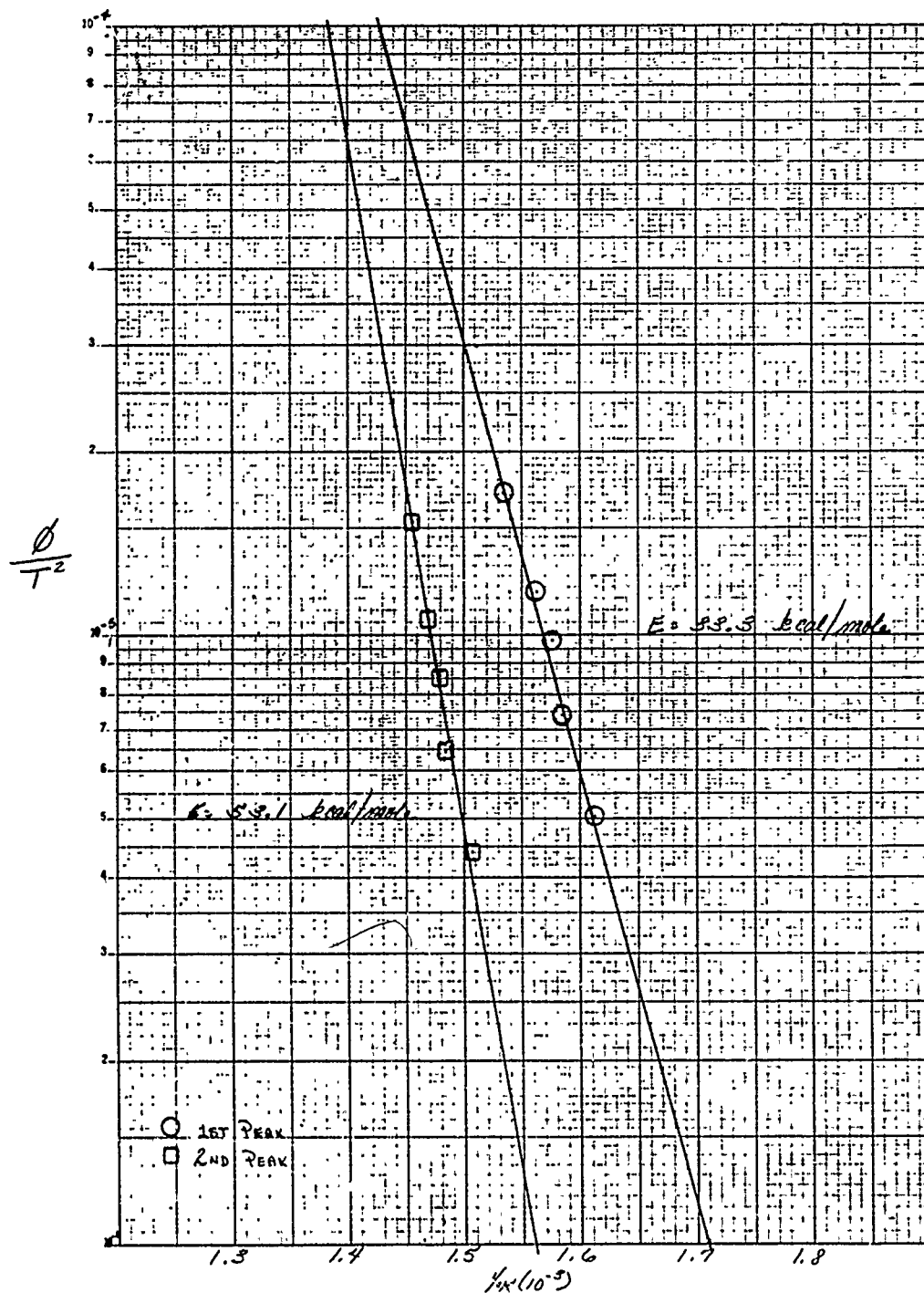


Figure 26. Plot of DTA Data, PL6670

TABLE VI. DTA Data on Propellant PL6670

A. For the activation energy (E) and frequency factor (A)

<u>Run No.</u>	<u>Peak No.</u>	<u>Exothermic Peak (°F)</u>	<u>Heating Rate (°F/min.)</u>	<u>E (kcal/mole)</u>	<u>A (sec⁻¹)</u>
3-43-2	1	657	3.5	33.3	4.1 X 10 ⁸
3-42-6		676	5.3		
3-46-4		682	7.1		
3-46-3		693	8.7		
3-41-2*		712	13.1		
3-46-2*		715	13.1		
3-43-2	2	735	3.5	53.1	2.9 X 10 ⁴
3-42-6		753	5.3		
3-41-6*		757	7.2		
3-46-4*		757	7.1		
3-42-3*		762	9.0		
3-46-3*		768	8.7		
3-41-2*		782	13.1		
3-46-2*		772	13.1		

*Similar heating rates were averaged together for the plot in Figure 26

B. For the specific rate constant (k)

<u>k(sec⁻¹)</u>		<u>Temperature (°F)</u>
<u>For 1st peak</u>	<u>For 2nd peak</u>	
8.4 X 10 ⁻⁸	2.9 X 10 ⁻¹¹	375
2.4 X 10 ⁻⁷	1.5 X 10 ⁻¹⁰	400
6.5 X 10 ⁻⁷	7.4 X 10 ⁻¹⁰	425
1.7 X 10 ⁻⁶	3.3 X 10 ⁻⁹	450
9.3 X 10 ⁻⁶	5.2 X 10 ⁻⁸	500
1.8 X 10 ⁻⁴	5.9 X 10 ⁻⁶	600

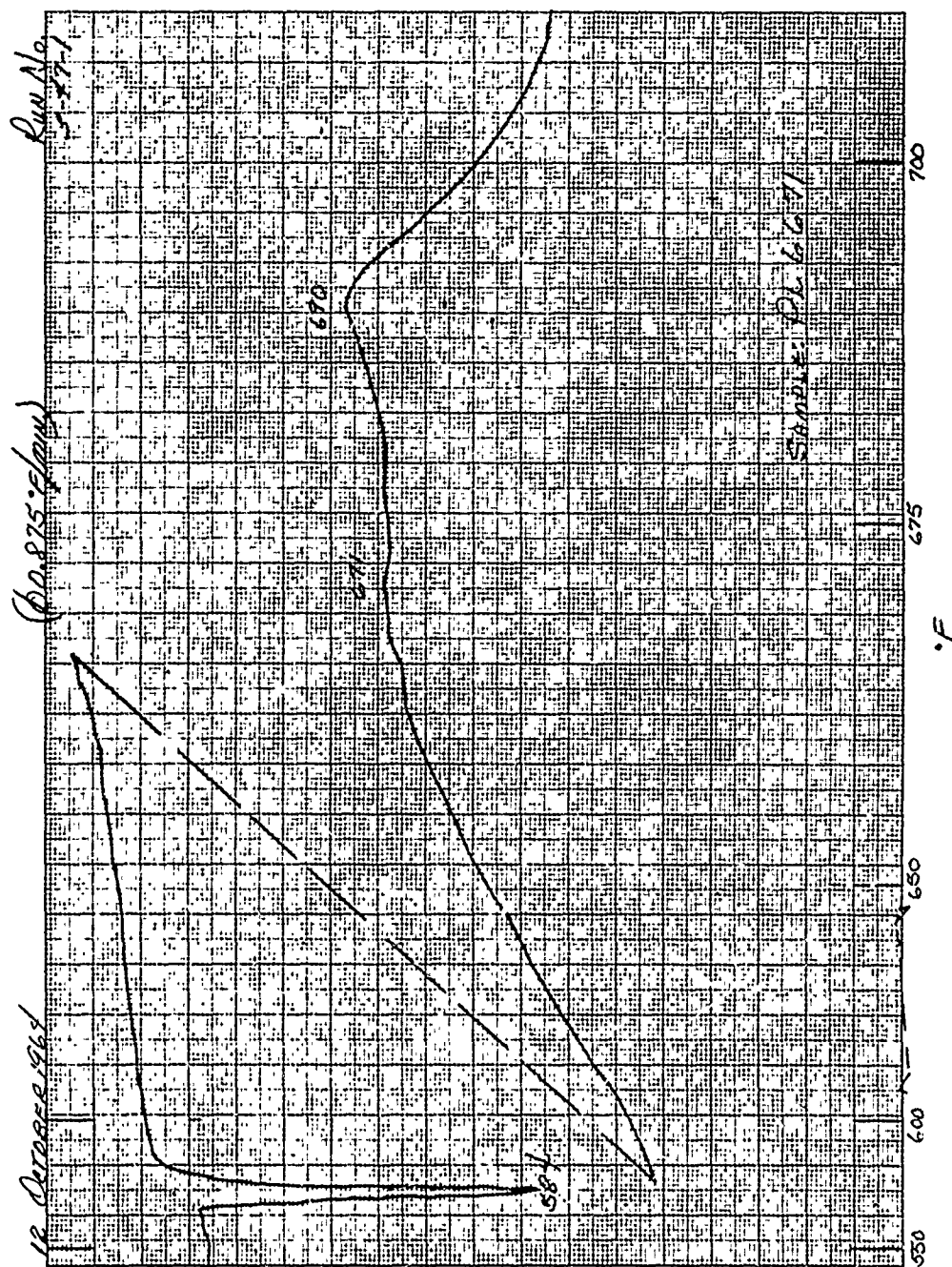


Figure 27. Thermogram, PL6671; $\dot{\Phi} = 0.875$ °F/min

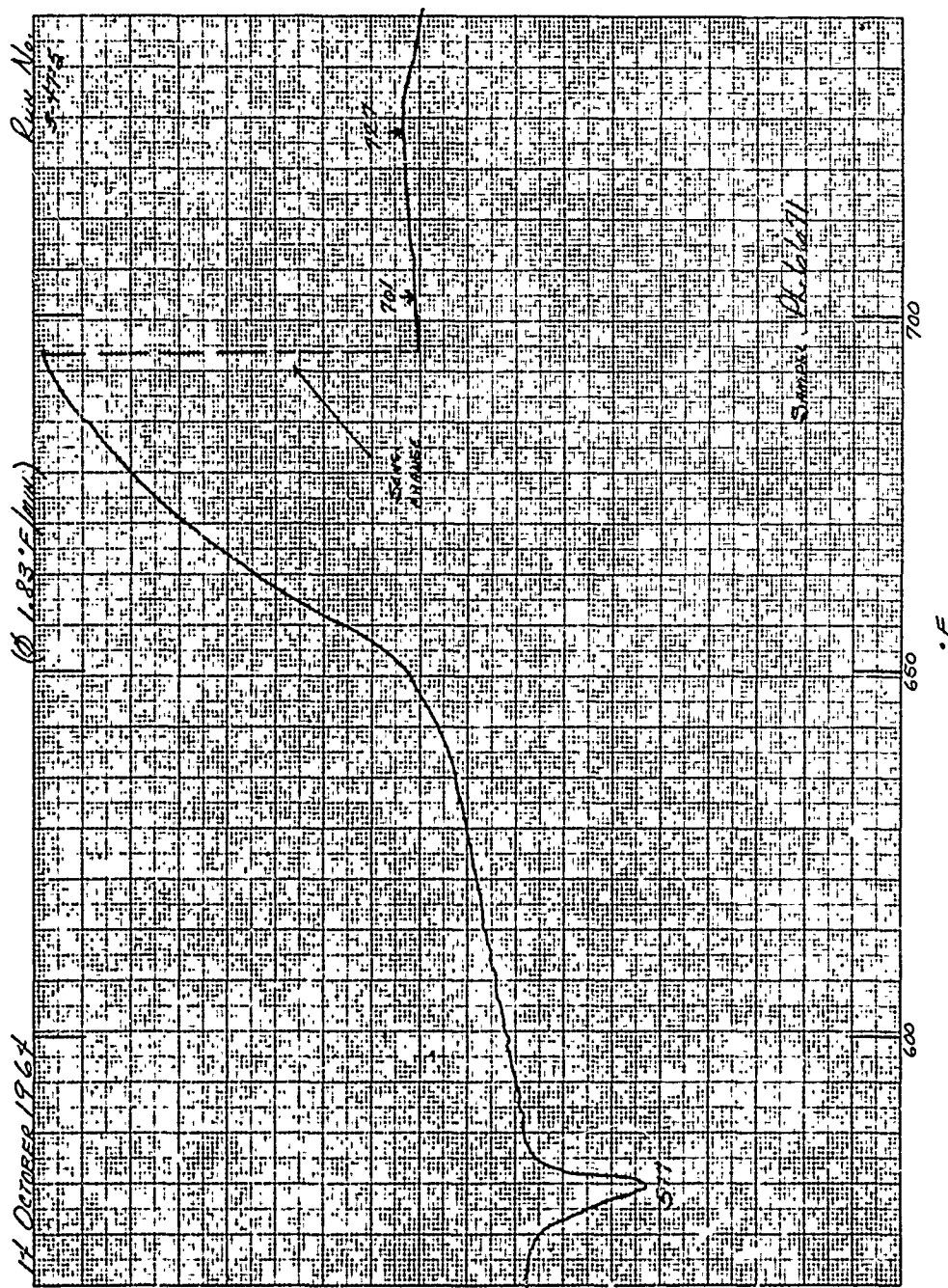


Figure 28. Thermogram, PL6671; $\Phi = 1.83$ °F/min

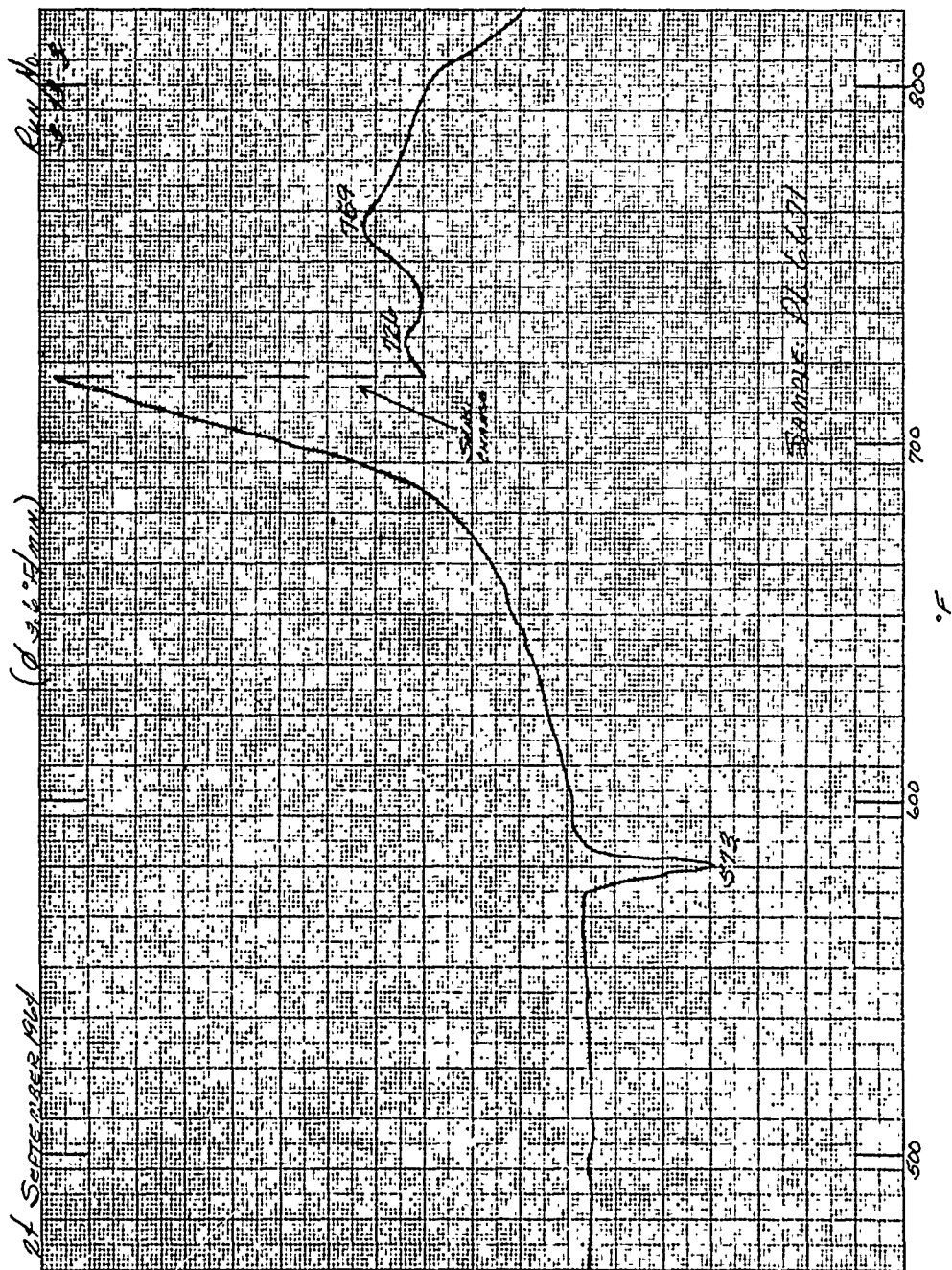


Figure 29. Thermogram, PL6671; $\Phi = 3.6$ °F/min

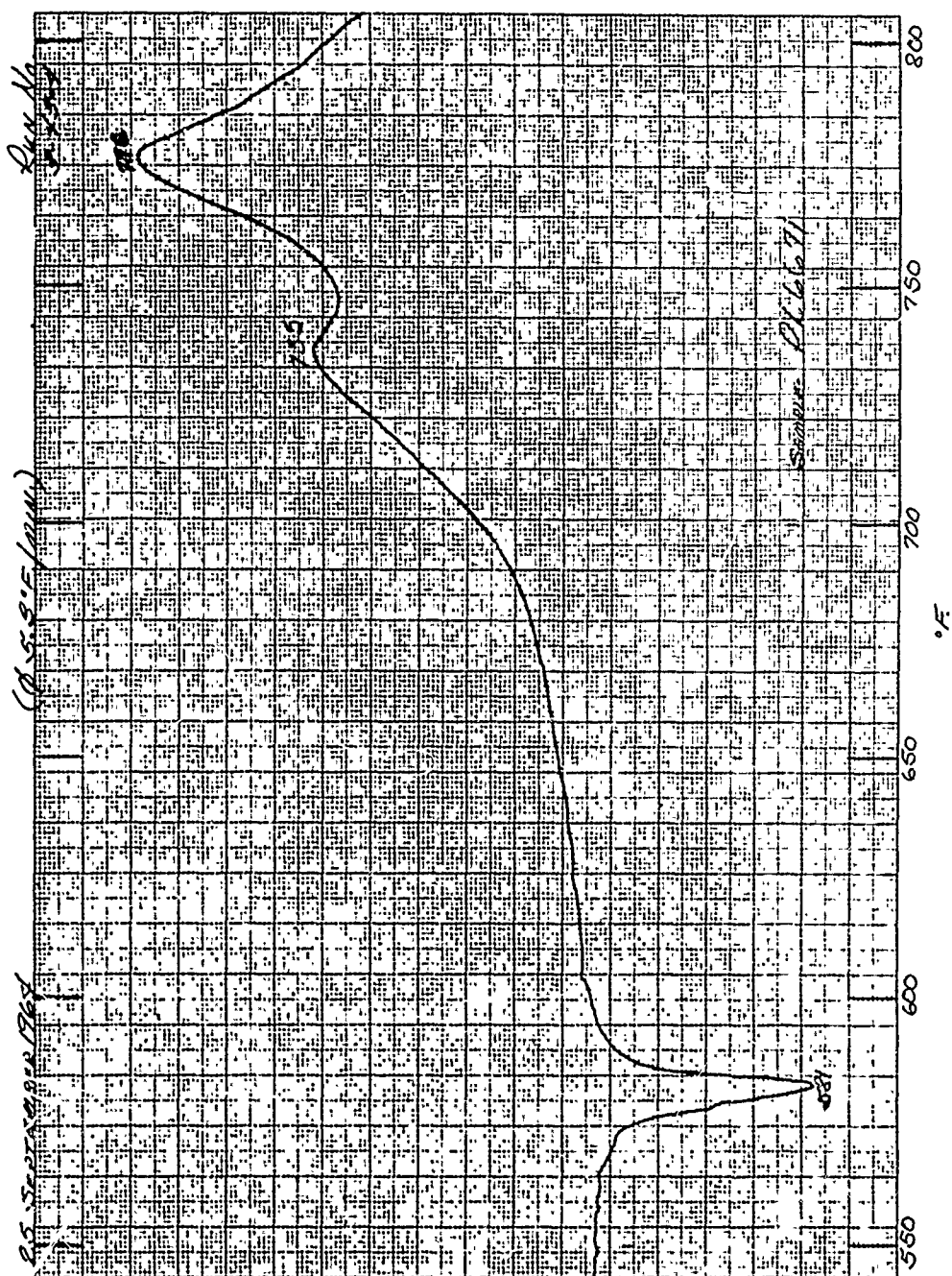


Figure 30. Thermogram, PL6671; $\Phi = 5.3$ °F/min

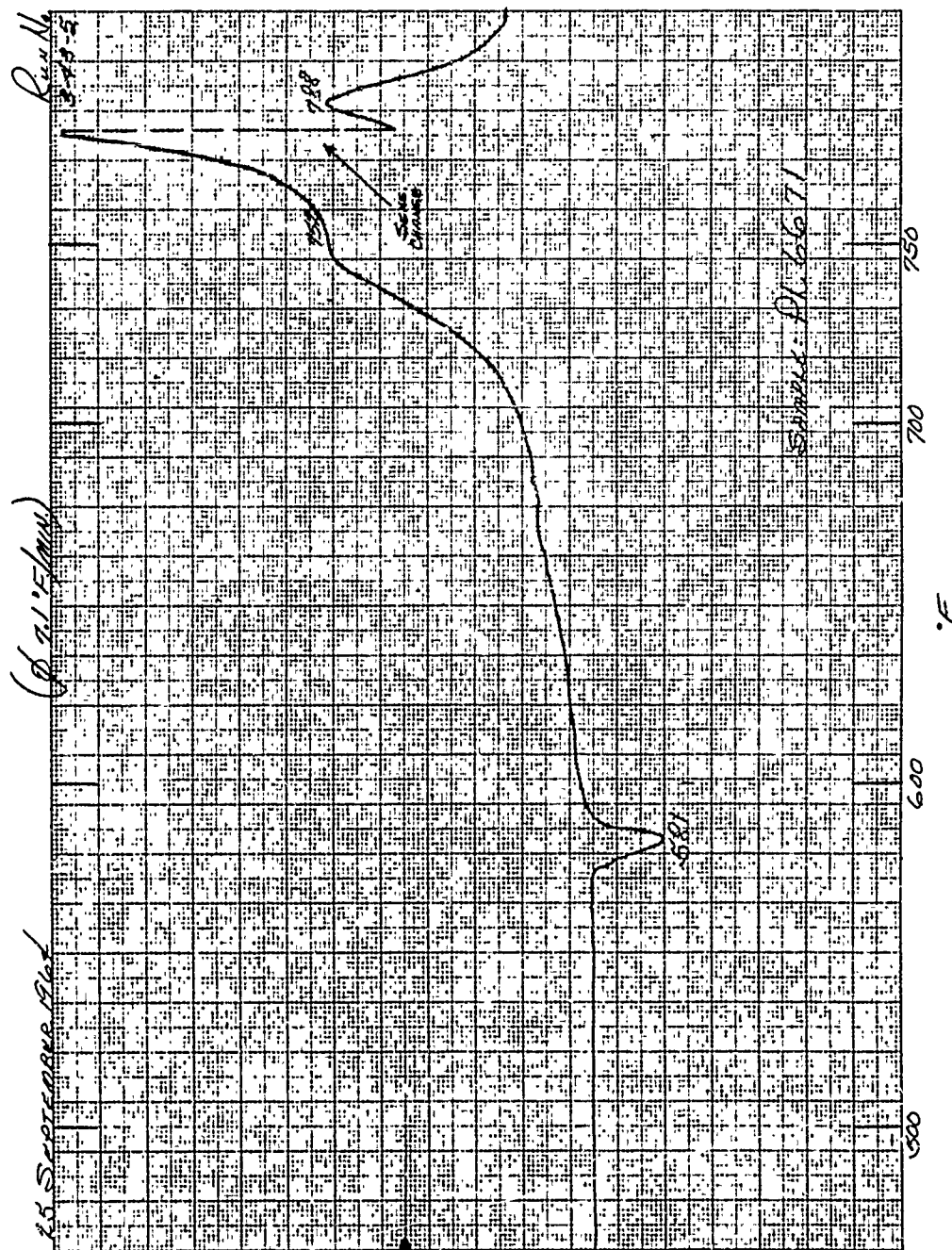


Figure 31. Thermogram, PL6671; $\Phi = 7.1$ °F/min

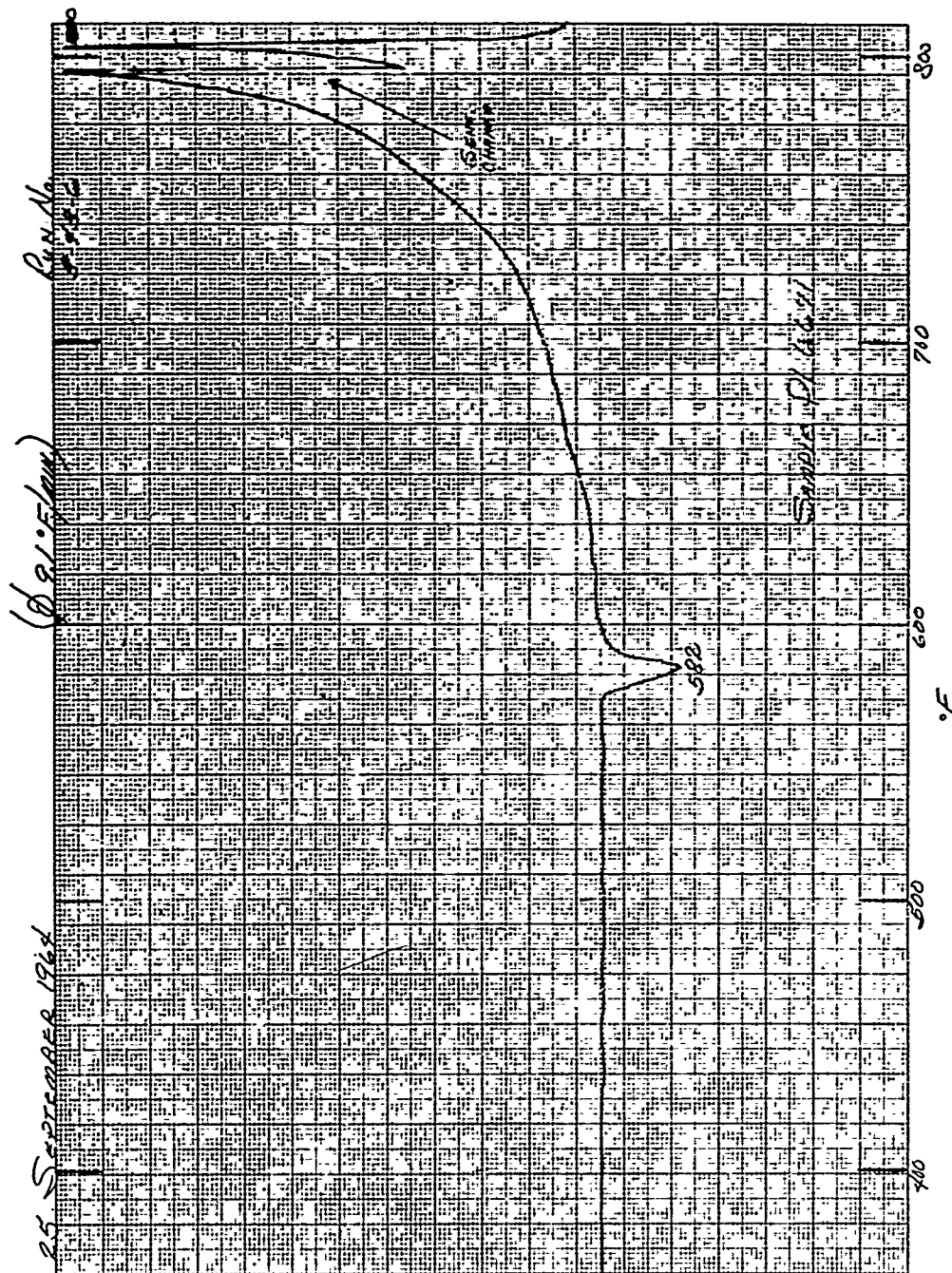


Figure 32. Thermogram, PL6671; $\Phi = 9.1^\circ\text{F/min}$

TABLE VII. DTA Data on Propellant PL6671

A. For the activation energy (E) and frequency factor (A)

<u>Run No.</u>	<u>Peak No.</u>	<u>Exothermic Peak (°F)</u>	<u>Heating Rate (°F /min.)</u>	<u>E (kcal/mole)</u>	<u>A (sec⁻¹)</u>
3-47-1	1	671	0.88	39.1	8.2 X 10 ⁹
3-47-5		701	1.83		
3-43-3		726	3.6		
3-43-4		735	5.3		
3-43-5		752	7.1		
3-47-1	2	690	0.88	32.2	1.7 X 10 ⁷
3-47-5		727	1.83		
3-43-3		759	3.6		
3-43-4		776	5.3		
3-43-5		788	7.1		
3-43-6		800	9.1		

B. For the specific rate constant (k)

<u>k(sec⁻¹)</u>		<u>Temperature (°F)</u>
<u>For 1st peak</u>	<u>For 2nd peak</u>	
3.1 X 10 ⁻⁹	1.2 X 10 ⁻⁸	375
1.1 X 10 ⁻⁸	3.2 X 10 ⁻⁸	400
3.4 X 10 ⁻⁸	8.3 X 10 ⁻⁸	425
1.0 X 10 ⁻⁷	2.1 X 10 ⁻⁷	450
7.8 X 10 ⁻⁷	1.1 X 10 ⁻⁶	500
2.5 X 10 ⁻⁵	1.9 X 10 ⁻⁵	600

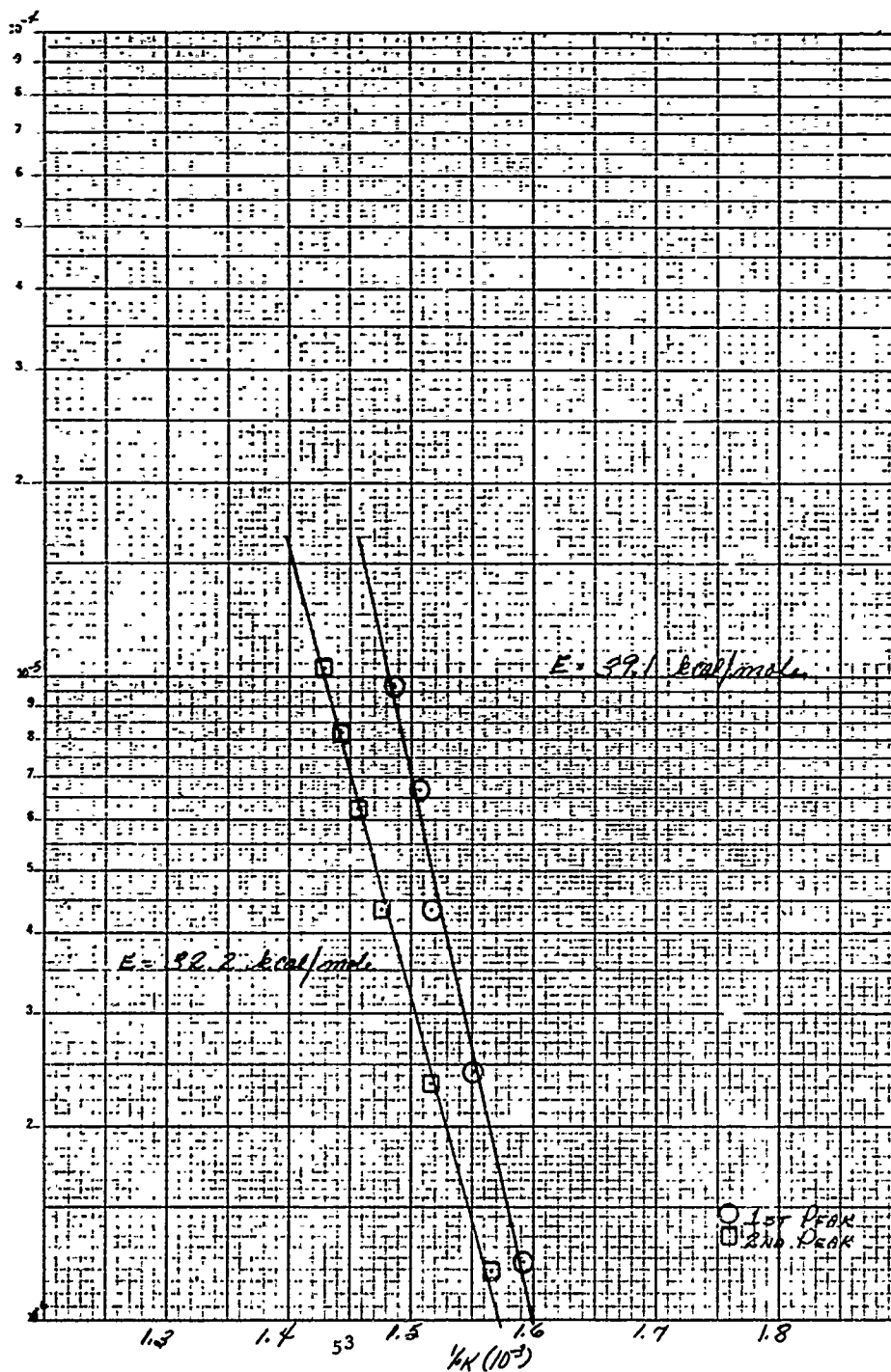


Figure 33. Plot of DTA Data, PL6671

where

- a = radius
- ρ = density
- Q = heat of reaction (explosion)
- λ = thermal conductivity
- δ = shape factor

and if the surface of the propellant grain, for a given geometry, is held at some temperature in excess of the critical temperature, the propellant grain will deflagrate after a given time.

The critical temperature was predicted for propellants PL6670 and PL6671 using the kinetic data from Tables VII and VIII with other physical and chemical data of the propellants. The results for solid cylinders are given in Table VIII for a comparison of propellant thermal stability.

In the isothermal analysis studies, samples of propellant were studied in two sizes, 0.25 and 3 inches in diameter. For the smaller samples, a quartz test tube (0.3 inch ID) in a tube-type Marshall furnace was used. For the larger samples, a standard cook-off oven was used. For a test, the oven was preheated to a selected temperature before placing the pre-weighed samples in the oven. The test was monitored remotely for a selected period of time, then the sample was removed from the oven, cooled, and reweighed for weight loss. The specific rate constant was determined from this weight loss study using the following equation

$$k = \frac{2.303}{t} \log \left[\frac{W_o}{W_x} \right] \quad (5)$$

where

- t = time
- W_o = initial weight
- W_x = weight after thermal aging

The activation energy could then be determined after several tests at selected temperatures from the slope of a plot of $\log k$ vs the reciprocal absolute temperature. The frequency factor could be determined from Equation 3.

The weight loss study on PL6670 propellant for the smaller samples was made in the temperature range of 425° to 552° F and for the larger samples the temperature was held constant

TABLE VIII. Predicted Critical Temperature (T_m) for Two Propellants
Based on DTA Data for Solid Cylinder.

Dia. of Grain (in.)	T_m ($^{\circ}$ F) of Propellant Type			
	PL6670		PL6671	
	1st peak	2nd peak	1st peak	2nd peak
1	488	596	552	560
2	446	563	512	510
5	396	523	463	450
12	353	488	420	400

at 400° F with preselected periods of time at 4, 17, and 50 hours. The larger samples showed very little weight change in the time studied, as shown in Table IX. These larger samples did show a change in color and very slight bulging after aging. The data on the smaller samples is given in Table IX with a plot of the data in Figure 34 for determining the activation energy. The frequency factor was determined from Equation 3 and the specific rate constant from Equation 5. The plot in Figure 34 shows a linear relationship over the range studied and a value for k at 400° F was predicted from this plot and is given in Table IX for a comparison with other data.

The weight loss study on PL6671 propellant for the smaller samples was made in the temperature range of 425° to 575° F and, for larger samples, the conditions were the same as for the PL6670 propellant. The larger samples showed no weight change in the time studied, but did show much darker change in color than the PL6670 propellant. The data on all the samples is given in Table IX. A plot of the data from the smaller samples is shown in Figure 35. A break in the plot is shown to occur at about 470° F, with activation energy above this temperature being 11.7 kcal per mole and below 470° F being 45.3 kcal per mole. Apparently, a different reaction path occurs above 470° F since the data show a linear relationship above and below this temperature in the temperature region studied. Values for k at 400° F were predicted from the lower slope plot and are given in Table IX.

The predicted specific rate constant from the small sample study for PL6670 was $2.4 \times 10^{-8} \text{ sec}^{-1}$ at 400° F, which compares well with the value of 1 to $3 \times 10^{-8} \text{ sec}^{-1}$ from the large sample study. The predicted specific rate constant for PL6671 was taken entirely from the small sample study because the weight loss of the larger sample was too small to be measured by present techniques. The weight loss rate of the PL6671 is only about one third that of PL6670 at 400° F.

The decomposition study by DTA in Table VIII shows the PL6671 to be more stable thermally than PL6670. The data from Table VIII indicate that a solid 5-inch diameter cylindrical grain of PL6670 or a solid 12-inch diameter cylindrical grain of PL6671 should not start to self-heat until about 400° F. This could be checked by isothermal analysis on the size in question for an experimental critical temperature and, also, to determine if the sample in question will explode or simply deflagrate on heating.

TABLE IX. Weight Loss Study of Two Propellants

A. For Specific Rate Constant (k)

<u>Weight (gm)</u>		<u>Oven Temp</u>	<u>Time</u>	<u>Weight Loss</u>	<u>k</u>
<u>Before</u>	<u>After</u>	<u>(°F)</u>	<u>(hr)</u>	<u>(%)</u>	<u>(sec-1)</u>
PL6670					
0.2988	0.2910	425	120.0	2.61	6.1 X 10 ⁻⁸
0.2771	0.2671	440	76.0	3.6	1.3 X 10 ⁻⁷
0.2702	0.2689	450	4.0	0.48	3.5 X 10 ⁻⁷
0.2753	0.2448	475	48.1	11.0	7.0 X 10 ⁻⁷
0.2766	0.2738	500	4.0	1.0	7.0 X 10 ⁻⁷
0.2941	0.2563	500	24.3	12.9	1.6 X 10 ⁻⁶
0.2800	0.2496	552	4.1	10.9	7.8 X 10 ⁻⁶
1620.	1620.	400	4.0	-	-
1630.	1627.	400	17.0	0.18	3 X 10 ⁻⁸
1627.	1624.	400	50.0	0.18	1 X 10 ⁻⁸

PL6671

0.3569	0.3517	425	139.0	1.5	2.9×10^{-8}
0.4179	0.4141	450	24.0	0.91	1.1×10^{-7}
0.3808	0.3678	455	71.0	3.4	1.4×10^{-7}
0.3880	0.3692	475	48.1	4.85	2.9×10^{-7}
0.3868	0.3738	500	24.0	3.4	4.0×10^{-7}
0.4588	0.4382	525	24.3	4.5	5.2×10^{-7}
0.3054	0.2982	550	4.0	2.4	1.7×10^{-6}
0.2325	0.2228	550	17.1	4.2	6.9×10^{-7}
0.3749	0.3560	575	17.0	5.0	8.5×10^{-7}
1937.	1935.	400	4.0	-	-
1930.	1930.	400	17.0	-	-
1932.	1932.	400	50.0	-	-

B. Activation Energy (E) and Frequency Factor (A) from the above data.

<u>Propellant</u>	<u>Temp Range</u> <u>(°F)</u>	<u>E</u> <u>(kcal/mole)</u>	<u>A</u> <u>(sec⁻¹)</u>
PL6670	425 - 575	37.2	2.6×10^9
PL6671	425 - 470	45.3	4.0×10^{12}
	470 - 575	11.7	2.4×10^{-2}

C. Predicted Specific Rate Constant (k) at 400° F from the above data.

<u>Propellant</u>	<u>Temp</u> <u>(°F)</u>	<u>k</u> <u>(sec⁻¹)</u>	<u>Predicted %</u> <u>Weight Loss</u>	<u>Time</u> <u>(hr)</u>
PL6670	400	2.4×10^{-8}	0.42	50
PL6670	400	2.4×10^{-8}	0.14	17
PL6670	400	2.4×10^{-8}	0.04	4
PL6671	400	7.5×10^{-9}	0.13	50
PL6671	400	7.5×10^{-9}	0.05	17
PL6671	400	7.5×10^{-9}	0.01	4

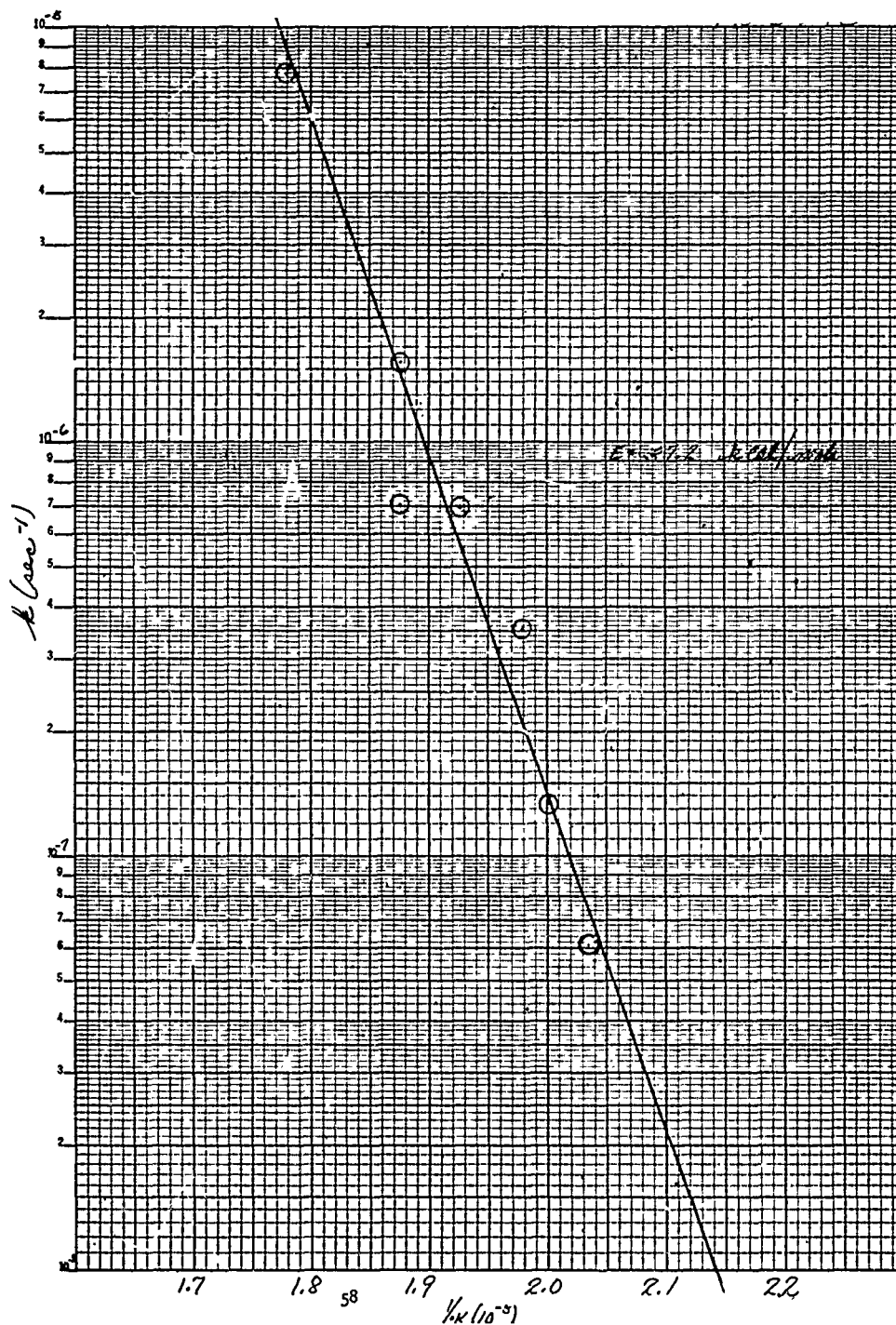


Figure 34. Rate Constant vs 1/Temperature, PL6670

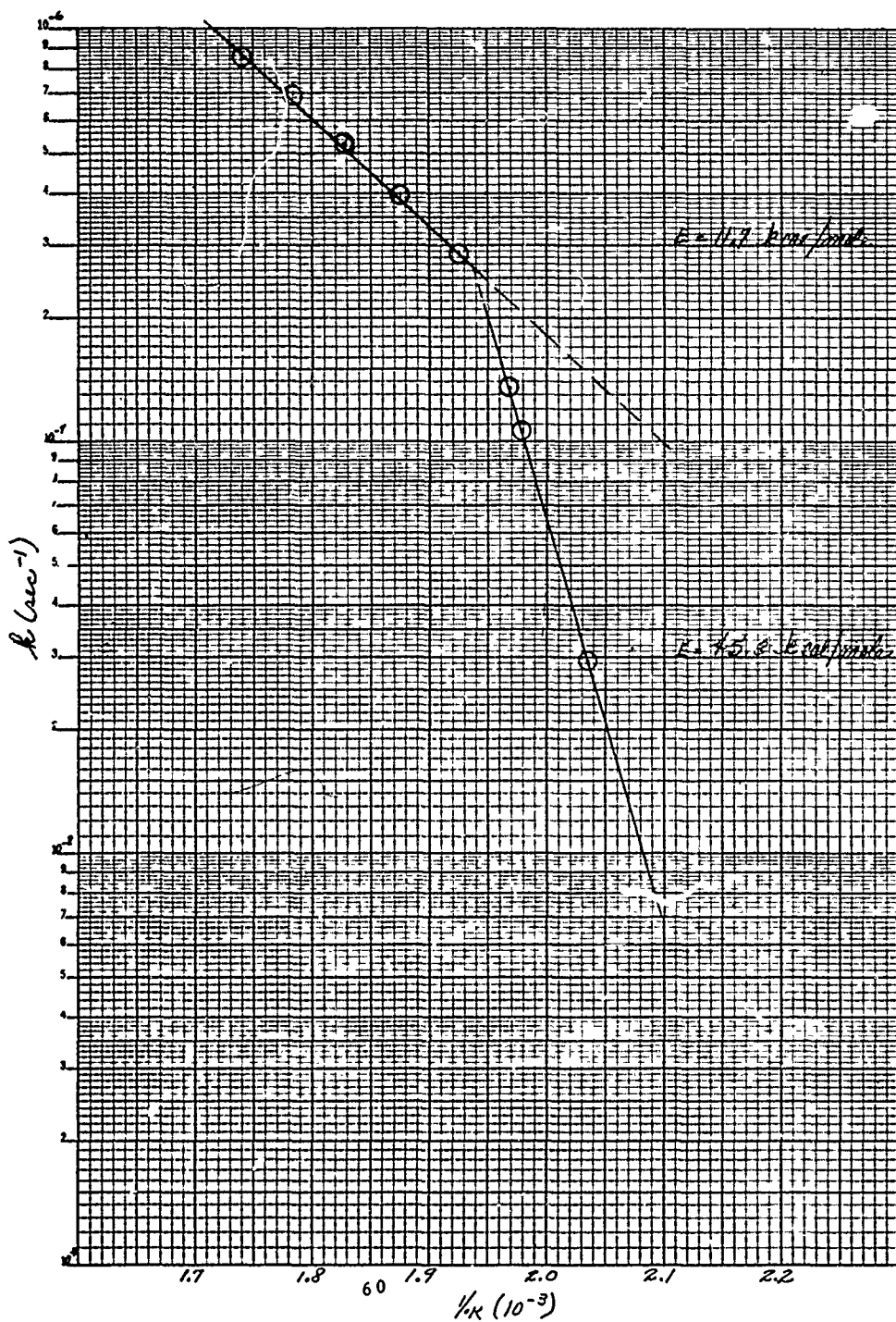


Figure 35. Rate Constant vs 1/Temperature, PL6671

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13. ABSTRACT Selected propellants for escape systems' rockets were investigated and evaluated at temperatures from -100°F to +400°F. AK14 Mod I propellant was successfully fired after conditioning for 108 hours between -100°F and +400°F (a cumulative time of 36 hours at 400°F). FL6670 propellant has had limited testing at 400°F. A KP-Hycar formulation has been scaled up in web but has not been tested. The test equipment especially designed and constructed for the program has performed reliably. This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the AFFDL (FDFR), Wright-Patterson AFB, Ohio 45433.			

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